Contemporary Food Engineering Series

Da-Wen Sun, Series Editor

# ADVANCES IN DEEP-FAT FRYING OF FOODS

Edited by

Serpil Sahin

Servet Gülüm Sumnu

CRC Press
Taylor & Francis Group

# ADVANCES IN DEEP-FAT FRYING OF FOODS

# Contemporary Food Engineering

**Series Editor**

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# *Dedication*

*To*

*Güler Özkan, Semra Şahin, Ayşe Demirezen and Ümit Burak Şahin*

*and*

*Deniz Sumnu Dindoruk*

# Contents

# Series Editor's Preface

## CONTEMPORARY FOOD ENGINEERING

Food engineering is the multidisciplinary field of applied physical sciences combined with knowledge of product properties. Food engineers provide the technological knowledge transfer essential to the cost-effective production and commercialization of food products and services. In particular, food engineers develop and design processes and equipment in order to convert raw agricultural materials and ingredients into safe, convenient, and nutritious consumer food products. However, food engineering topics are continuously undergoing changes to meet diverse consumer demands, and the subject is being rapidly developed to reflect market needs.

In the development of food engineering, one of the many challenges is employing modern tools and knowledge, such as computational materials science and nanotechnology, to develop new products and processes. Simultaneously, improving food quality, safety, and security remain critical issues in food engineering study. New packaging materials and techniques are being developed to provide more protection to foods, and novel preservation technologies are emerging to enhance food security and defense. Additionally, process control and automation regularly appear among the top priorities identified in food engineering. Advanced monitoring and control systems are developed to facilitate automation and flexible food manufacturing. Furthermore, energy saving and minimization of environmental problems continue to be important food engineering issues while significant progress is being made in waste management, efficient utilization of energy, and reduction of effluents and emissions in food production.

Consisting of edited books, the *Contemporary Food Engineering* book series attempts to address some of the recent developments in food engineering. Advances in classical unit operations in engineering applied to food manufacturing are covered as well as such topics as progress in the transport and storage of liquid and solid foods; heating, chilling, and freezing of foods; mass transfer in foods; chemical and biochemical aspects of food engineering and the use of kinetic analysis; dehydration, thermal processing, nonthermal processing, extrusion, liquid food concentration, membrane processes and applications of membranes in food processing; shelf-life, electronic indicators in inventory management, and sustainable technologies in food processing; and packaging, cleaning, and sanitation. The books are aimed at professional food scientists, academics researching food engineering problems, and graduate-level students.

The editors of the books are leading engineers and scientists from many parts of the world. All the editors were asked to present their books in a manner that would address the market's need and pinpoint the cutting-edge technologies in food engineering. Furthermore, all contributions are written by internationally renowned experts with both academic and professional credentials. All authors have attempted

to provide critical, comprehensive, and readily accessible information on the art and science of a relevant topic in each chapter, with reference lists to be used by readers for further information. Therefore, each book can serve as an essential reference source to students and researchers in universities and research institutions.

**Da-Wen Sun, Series Editor**

# Preface

Deep-fat frying is a complex process. It involves heat and mass transfer between food and the frying medium. This book explains the frying process by combining engineering principles with knowledge of biochemistry. The editors aim to provide recent references about frying that will be helpful for researchers and food processors working in the field of frying. This book will also be useful to students taking courses related to unit operations in the food industry.

The history of various fried products and general information about frying are given in the introduction. The second chapter reviews heat and mass transfer phenomena, mainly focusing on the adhesion and capillary migration of oil during the cooling period. Convective heat transfer from oil to the product, convective heat transfer coefficient during frying, coupled heat and mass transfer inside the product, and the mechanism of oil uptake will be discussed in this chapter. A series of reactions take place during frying in oil or fat that is exposed to high temperature in air and moisture. As a result, the quality of the frying oil and of the fried food is lost. The factors affecting the quality of frying oil, the main changes taking place in the frying oil, the methods used for determination of oil degradation, the antioxidants that can be used to retain the quality of frying oil, and the interactions between the food and the frying oil are given in Chapters 3 and 4.

Kinetic studies of the quality changes during frying that predict and improve the final quality of the product are summarized in Chapter 5. Moisture and oil contents, color, texture, volume, porosity and acrylamide content are considered as quality parameters.

It is important to have the physical properties data of fried foods because they affect the rate of heat and mass transfer during frying. Physical properties of food products change significantly during frying, and a change in one physical property affects the others. Variations in geometric, optic, mechanic, thermal and mass transfer properties in various foods during frying are given in Chapter 6.

Acrylamide, which is a potential carcinogen formed during processing at high temperatures, is a recent safety concern in fried products. Therefore, in Chapter 7 the mechanism of acrylamide formation and the factors to reduce its formation are discussed, and the studies related to acrylamide in frying are summarized.

It is not enough to study the changes in deep-fat frying at the macroscopic level. It is also important to examine microstructural changes in fried products. During frying, water vapor is formed due to high temperature and is transferred through the surface of the product due to pressure and concentration gradients. As a result, crust is formed and pores are developed. Pores affect oil absorption. In addition, shrinkage may be observed. In Chapter 8, microstructural changes during frying and the techniques used to study food microstructures are reviewed. The relation between the quality and microstructural changes is also discussed.

The desirable flavor formed during frying is unique. That is, it is not developed during other cooking methods. The flavors in frying oils may come from natural

compounds, processing, and/or degradation of fatty acids. Sources of flavor, development of flavor during frying, and measurement of deterioration products related to flavor are discussed in Chapter 9.

The consumption of battered and breaded foods in the frying market is increasing. Different batter formulations are employed to obtain the desired quality. In general, there is a correlation between the rheological behavior of batters and product quality. Therefore, studying rheological properties of different batter formulations will provide insights into the final fried product quality. Studies about the rheological properties of batters are given in Chapter 10, and the variations of physical properties of battered fried products (batter adhesion, color and texture) are discussed in Chapter 11. Sensory analysis of battered foods is also mentioned.

In Chapter 12, the importance of industrial frying, the evolution of the frying industry, types of fryers, criteria for fryer selection, and processes for different fried products are summarized. In addition, the terminology used in industrial frying is given.

There is much ongoing research and recent developments in frying technologies due to increasing consumer demand for low-fat and low-acrylamide products without losing product quality. In Chapter 13, the principles of vacuum, microwave and pressure frying are mentioned, and recent studies about these alternative technologies are discussed.

**Serpil Sahin**
**Servet Gülüm Sumnu**

# Series Editor



Born in Southern China, Professor **Da-Wen Sun** is a world authority on food engineering research and education. His main research activities include the cooling, drying, and refrigeration processes and systems, quality and safety of food products, bioprocess simulation and optimization, and computer vision technology. Of special interest are his innovative studies on vacuum cooling of cooked meats, pizza quality inspection by computer vision, and edible films for shelf-life extension of fruits and vegetables which have been widely reported in national and international media. Results of his work have been published in over 180 peer-reviewed journal papers and more than 200 conference papers.

He received first class B.Sc. Honors and M.Sc. degrees in mechanical engineering, and a Ph.D. in chemical engineering in China before working in various universities in Europe. He became the first Chinese national to be permanently employed in an Irish University when he was appointed college lecturer at National University of Ireland, Dublin (University College Dublin), in 1995, and was then continuously promoted in the shortest possible time to senior lecturer, associate professor, and full professor. Sun is now professor of Food Biosystems Engineering and director of the Food Refrigeration and Computerized Food Technology Research Group in University College Dublin.

As a leading educator in food engineering, Sun has contributed significantly to the field of food engineering. He has trained many Ph.D. students, who have made their own contributions to the industry and academia. He has also, on a regular basis, given lectures on advances in food engineering in academic institutions internationally and delivered keynote speeches at international conferences. As a recognized authority in food engineering, he has been conferred adjunct/visiting/consulting professorships from ten top universities in China including Zhejiang University, Shanghai Jiaotong University, Harbin Institute of Technology, China Agricultural University, South China University of Technology, and Jiangnan University. In recognition of his significant contribution to food engineering worldwide and for his outstanding leadership in the field, the International Commission of Agricultural Engineering (CIGR) awarded him the CIGR Merit Award in 2000 and again in 2006 and the Institution of Mechanical Engineers (IMechE) based in the United Kingdom named him Food Engineer of the Year 2004. In 2008 he was awarded the CIGR Recognition Award for his distinguished achievements in the top one percent of agricultural engineering scientists around the world.

He is a Fellow of the Institution of Agricultural Engineers. He has also received numerous awards for teaching and research excellence, including the President's Research Fellowship, and he twice received the President's Research Award of University College Dublin. He is a member of the CIGR Executive Board and Honorary Vice-President of CIGR, editor-in-chief of *Food and Bioprocess Technology—An International Journal* (Springer), series editor of the "*Contemporary Food Engineering*" book series (CRC Press/Taylor & Francis), former editor of *Journal of Food Engineering* (Elsevier), and editorial board member for *Journal of Food Process Engineering* (Blackwell), *Sensing and Instrumentation for Food Quality and Safety* (Springer), and *Czech Journal of Food Sciences*. He is also a chartered engineer registered in the UK Engineering Council.

# Editors

**Serpil Sahin** is a professor in the Department of Food Engineering, Middle East Technical University, Ankara, Turkey. She has authored or co-authored 45 journal articles and book chapters. She is one of the authors of *Physical Properties of Foods* (2006, Springer) and one of the editors of *Food Engineering Aspects of Baking of Sweet Goods* (Volume II in Contemporary Food Engineering Series, published by Taylor and Francis). She received BS (1989), MS (1992), and PhD (1997) degrees from the Department of Food Engineering, Middle East Technical University. Sahin was a visiting scholar in the Department of Food, Agricultural and Biological Engineering at the Ohio State University for one year (1996). She is working on food processes, especially frying, baking, separation processes, and applications of microwaves.

**Servet Gülüm Sumnu** is a professor in the Department of Food Engineering, Middle East Technical University, Ankara, Turkey. She has authored or co-authored 55 journal articles and book chapters. She is one of the authors of *Physical Properties of Foods* (2006, Springer) and one of the editors of *Food Engineering Aspects of Baking of Sweet Goods* (Volume II in the Contemporary Food Engineering Series, published by Taylor and Francis). She received BS (1991), MS (1994), and PhD (1997) degrees from the Department of Food Engineering, Middle East Technical University. Sumnu was a visiting scholar in the Department of Food Science and Technology at the Ohio State University for one year (1996). She is working on microwave food processes, especially microwave baking and frying. Her research also focuses on the physicochemical properties of hydrocolloids and the determination of physical properties of foods.

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# 1 Introduction

*Serpil Sahin and Servet Gülüm Sumnu*

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## 1.1 HISTORY OF FRIED PRODUCTS

Frying is one of the oldest food preparation processes. It dates back as early as 1600 BC. Various fried products have been consumed by different cultures during the centuries. Some fried products are only traditional, but one product that is consumed throughout the world is fried potatoes, also known as "French fries." How fried potatoes were named French fries is interesting. It is thought that the inventors of French fries were Belgians. The Belgian historian Jo Gerard stated that potatoes cut lengthwise had been fried in 1680 in the Spanish Netherlands (region between Dinant and Liege in Belgium) when local people were unable to fish during the winter. During World War I, American soldiers in Belgium ate Belgian fried potatoes for the first time. They called these fried potatoes "French fries" because the official language of the Belgian army was French.

The inventor of potato chips was George Crum. He was a Native American chef in a hotel and discovered potato chips by accident. A customer at the hotel ordered fried potatoes, but he did not like the thickness of the French fries. He kept returning the order to the chef. Mr. Crum became bored with the complaints; he sliced the potatoes very thin and fried them until a very crisp texture was obtained. Unexpectedly, the customer liked them so much that potato chips became famous in the menu of the hotel.

The snacks that are competing with potato chips in the USA are tortilla and corn chips. The main difference between tortilla and corn chips is that tortilla chips are baked before frying, whereas corn chips are fried without baking. The traditional method to produce tortillas from corn was developed by Aztec Indians in the central region of Mexico. The process of transforming corn to masa is known as "nixtamalization," and involves boiling, quenching and steeping of corn into lime solution. After the liquor obtained from steeping is discarded, the cooked corn is washed to remove the excess lime and loose pericarp, and then stone ground to produce masa. Tortilla chips were first mass produced in Los Angeles in 1940s.

The origin of fried chicken is the southern states of America. Fried chicken had been in the diet of Scottish people for a long time, but they did not use seasoning. After African slaves had been hired as cooks, they added seasoning to the fried chicken of Scottish people. Because slaves were allowed to feed only chickens, fried

chicken became the dish that they ate on special occasions. This tradition spread to all African-American communities after the abolition of slavery.

Poultry, seafood and red meat coated with batters and breading prior to frying are available in the market. Batters are liquid mixtures containing mainly water, flour and seasoning, but their formulations vary greatly. Batters can be categorized into interface/adhesion and puff/tempura. The interface/adhesion batters are used with breading, and act as an adhesive layer between the surface of the product and breading. No chemical leavening is used in this type of batter. Puff/tempura batters are used as an outer coating of the food and contain leavening agents. Tempura batter was introduced to Japan by Portuguese visitors.

There are different fried dough products throughout the world. Doughnut is one kind that has different names and is consumed in many countries. Doughnuts are of two types: yeast leavened and chemically leavened. Chemically leavened doughnuts are known as "cake doughnuts." Yeast-leavened doughnuts absorb more oil than chemically leavened doughnuts because they are fried longer. However, additional fat is included to the batter of chemically leavened doughnuts. There are different theories about the inventors of doughnuts. According to one theory, doughnuts came to North America by Dutch settlers because they were also known to be the inventors of other popular American desserts or pastries. However, there is evidence that pastries were also prepared by Native Americans.

After people became conscious of the health problems arising from consumption of high-fat-containing fried products, studies on how to reduce the fat content of these products started. One of the important developments in this area was the production of Olestra by Procter and Gamble Company (Cincinnati, OH, USA). Olestra, which is a sucrose polyester, is indigestible. Olestra was approved by the USA Food and Drug Administration (FDA) in 1996. Potato and tortilla chips fried in Olestra were marketed by Frito Lay. Although these products were promising, consumers did not accept them because they had side effects such as gastrointestinal disorders and diarrhea.

## 1.2 GENERAL INFORMATION ABOUT FRYING

Deep fat frying is a simultaneous heat and mass transfer process. Heat transfer is by convection between the oil and the food surface, and by conduction within the food. When the food is immersed in hot oil, water vapor is formed due to high temperature, and it is transferred through the surface of the product due to pressure and concentration gradients. As a result, crust is formed and pores are developed. Characteristic hydrophilicity of the raw sample is lost as the crust is developed, which results in a higher rate of oil absorption. Pores affect oil absorption. Oil enters into pores provided by moisture loss mainly during the cooling stage. In addition, shrinkage may be observed during frying. It is important to examine these changes at the micro level.

Variation of the physical properties of food products during frying should be known because they affect the rate of heat and mass transfer during frying. Geometric properties such as shape, size, surface area, volume and density of foods change during frying. Due to changes in composition (moisture and oil content),

temperature and porosity, thermal properties also change during frying. Convective heat transfer coefficient changes with oil temperature and oil degradation. It also changes during frying, and it is different at the top and bottom surfaces of the product due to the effect of steam bubbling. Changes in pore structure influence moisture diffusivity and oil uptake. Moisture diffusivity is also affected by frying time, temperature, and product moisture content.

Biochemical changes in food material being fried and also in frying oil or fat are important in frying. The characteristic color and flavor of the fried product is provided by Maillard reactions in the crust. The formation of acrylamide, which is a potential carcinogen, is also linked to Maillard reactions. Gelatinization of starch, denaturation of proteins, inactivation of enzymes, and destruction of microorganisms are also observed in the product being fried depending on its constituents, as in other food processes (e.g., drying, baking). However, various flavor components found in fried products are not developed during other cooking methods such as baking.

Frying is a complex process. The coupling between reactions and heat and mass transfer are poorly understood. Simultaneous transfer of heat and mass, and oil uptake, in addition to moisture loss, make the engineering calculations more complex.

Oil is exposed to high temperature in air and moisture during frying. A number of chemical reactions such as hydrolysis, and oxidative and thermal degradations take place under these conditions. Consequently, the quality of the frying oil and of the fried food is lost. Some desirable chemical compounds are also formed in the oils during frying. It is important to assess the quality of oil because it is absorbed by the food and becomes part of the product.

Frying temperature and time, surface area of the material being fried, and usage of pretreatments such as blanching, drying, coating, or immersion in sugar solutions affect the quality of the product. Moisture content, oil content, acrylamide content, density, porosity, shrinkage, color and texture are the most important quality parameters in fried products. Studying the kinetics of the quality changes during frying is necessary to predict and improve the final quality of the product.

Reduction of oil uptake is the main concern of researchers who wish to satisfy the health demands of consumers. Coating of potatoes with hydrocolloids and/or modified starches is an alternative way to reduce oil uptake during frying. Incorporation of powdered cellulose or cellulose derivatives into batters or doughnut mixes reduces oil uptake due to their thermal gelation and film-forming properties. There are various studies in which batters and breading with different compositions were used to reduce the oil content of fried products. In addition, alternative frying technologies such as vacuum, pressure or microwave frying to reduce the oil content of these products appear promising.

# 2 Heat and Mass Transfer During Frying

*Nawel Achir, Olivier Vitrac, and Gilles Trystram*

## CONTENTS



## 2.1 INTRODUCTION

Deep frying is one of the oldest processes to dry, to cook and to formulate food products (Varela 1998; Gertz 2000): various roots and tubers (Gamble and Rice 1987; Baumann and Escher 1995; Vitrac et al. 2001, 2002), fruits (Diaz et al. 1999) and meat (Lisse and Raoult-Wack 1998). Its use has been extended to dry and roast coffee, to dry and structure oily products prior to pressing (Grewal 1996; Hounhouigan et al. 1997) and also enlarged to non-food applications, including the drying and formulation of timber (Baillères et al. 2001) and sludge (Silva, Rudolph, and Taranto 2005). Its success comes from its versatility and flexibility at the industrial and household scale. Besides, it offers several advantages which are difficult to reproduce with alternative technologies: very efficient heat transfer, crispy texture associated with rapid drying, and tasteful fried products (Raoult-Wack et al. 2000; Pedreschi and Moyano 2005). However, frying has several limitations: (i) difficulty to orient

independently heat- and water-mediated phenomena that occur simultaneously during frying; and (ii) increased consumer demand for low-fat products.

This chapter reviews the heat and mass transfer phenomena that control the heating and drying of products during frying, and the physical phenomena that control oil adhesion and oil capillary migration during cooling. The first section examines how steam bubbling at the oil–food product interface intensifies or alleviates convective heat transfer. The second section analyzes heat and mass transfer at the scale of the food product. The effect of the initial product composition and structure is discussed according to phenomena which are critical for the thermal history of food products: the internal liquid transport of water, and the desorption isobar of water in the hygroscopic domain. The third section details the mechanism of oil uptake at the scale of the material and at the scale of the cell structure. The last section presents a simplified, but nevertheless realistic, model of coupled heat and mass transfer which can be used for thin (chips) or thick (French fries) geometries.

## 2.2 PHYSICAL PRINCIPLES OF DEEP-FRYING AT PROCESS SCALE

### 2.2.1 Convective Heat Transfer from the Oil to the Product

During deep frying, heat and mass transfer in the product and product evolution are governed by heat transferred from oil to the product by its external surface. The impact of heating is related to the final reached temperature and to the rate of heating. The main originality of deep frying (Figure 2.1) is to transfer heat at a very high rate using the heat reservoir created by the large volume of oil compared with

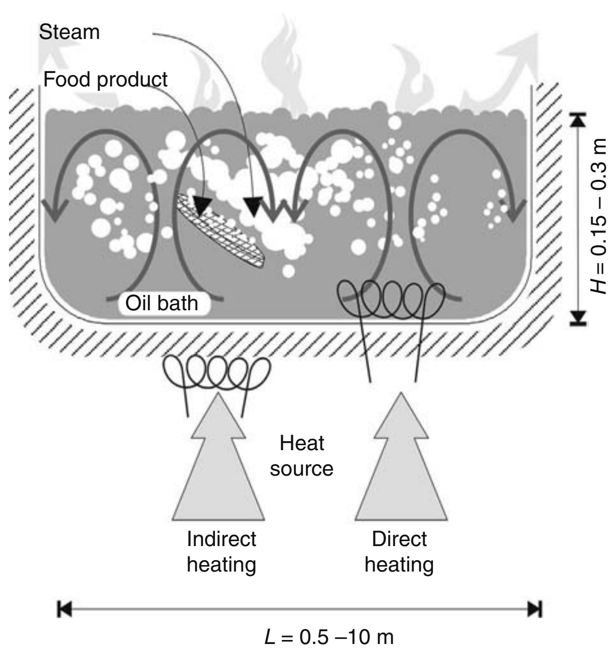



**FIGURE 2.1** Principle of convective heat transfer during deep frying.

the product. Due to the density and heat capacity of oil, involved heat transfer rates are in particular higher than those encountered with other heat vectors such as gas (e.g., hot air, superheated steam). Besides, when the product is surrounded with oil (immersed product), heat is transferred almost uniformly to the product. This feature is more difficult to achieve with alternative cooking or drying processes such as pan-frying and infrared heating.

Deep frying uses a large volume of liquid with a high boiling point, such as oil, fat and paraffin, whose initial temperature is set significantly above the boiling point of free water. This process can be done in batch or in continuous form using an immersed conveyor. Because oil and fats are highly thermo-expandable fluids, buoyancy forces are particularly efficient to homogenize the temperature along the vertical direction.

The physical processes are similar in household and industrial processes, only the ways how temperature is controlled are different. As depicted in Figure 2.2 on an experimental deep-fryer, heat is mainly used to vaporize water. Steam bubbles escaping from the product external surface are observed immediately or a few seconds after immersion into hot oil. Because steam is then the only gas phase in the product, vaporization of free water occurs at the saturation temperature of water, noted $T_{sat}$, and the vaporization rate is roughly proportional to the temperature difference between the oil bulk and $T_{sat}$. Experimentally, changing the oil temperature so that the oil temperature is lower than the surface product temperature makes bubbling disappear. Increasing the external pressure or the internal pressure so that the boiling point of water is higher than the oil temperature suppresses the vaporization.

The decrease in bubbling observed during frying is associated with a lower driving force due to the surface heating of the product. Drying occurs while the surface temperature of the product is lower than the oil bulk. When the product is at thermal equilibrium with oil, there is still water in the product. Indeed, increasing the oil temperature leads again to bubbling until a new thermal equilibrium is reached. Thus, at a given pressure (conventionally at atmospheric pressure), the bulk oil temperature enforces the minimum residual water content, which corresponds to the saturation temperature of water in equilibrium with solutes and macromolecules. The concept of isobaric desorption isotherm will be detailed in Section 2.3.2.

Convective heat fluxes during deep frying of thin products (e.g., chips) have been studied from a macroscopic heat balance at the scale of the deep fryer (Vitrac, Trystram, and Raoult-Wack 2003). The variation of oil bulk temperature was identified as heat losses, heat absorbed by the wired basket, and finally as convective heat flux transferred to the product, noted $q_C$. Figure 2.3 summarizes the principles of measurements and the typical kinetic of $q_C$ assessed during the frying of 1.5-mm thick cassava chips fried at 160°C in palm oil. During the same experiment, the core temperature, $T_C$, was also measured.

The kinetic of $q_C$ was associated to three regimes (Figure 2.3e). The very early first transitory regime (regime A) is associated with very high convective heat fluxes of up to 150 kW.m$^{-2}$, and is followed by a slug flow of steam bubbles. When the generation of steam is faster than the ability of the medium to remove steam, $q_C$ decreases down to almost zero due to the heat transfer resistance by steam film around the product. Because the core temperature remains below the saturation temperature, the initial vaporization regime is related to the surface vaporization of water.

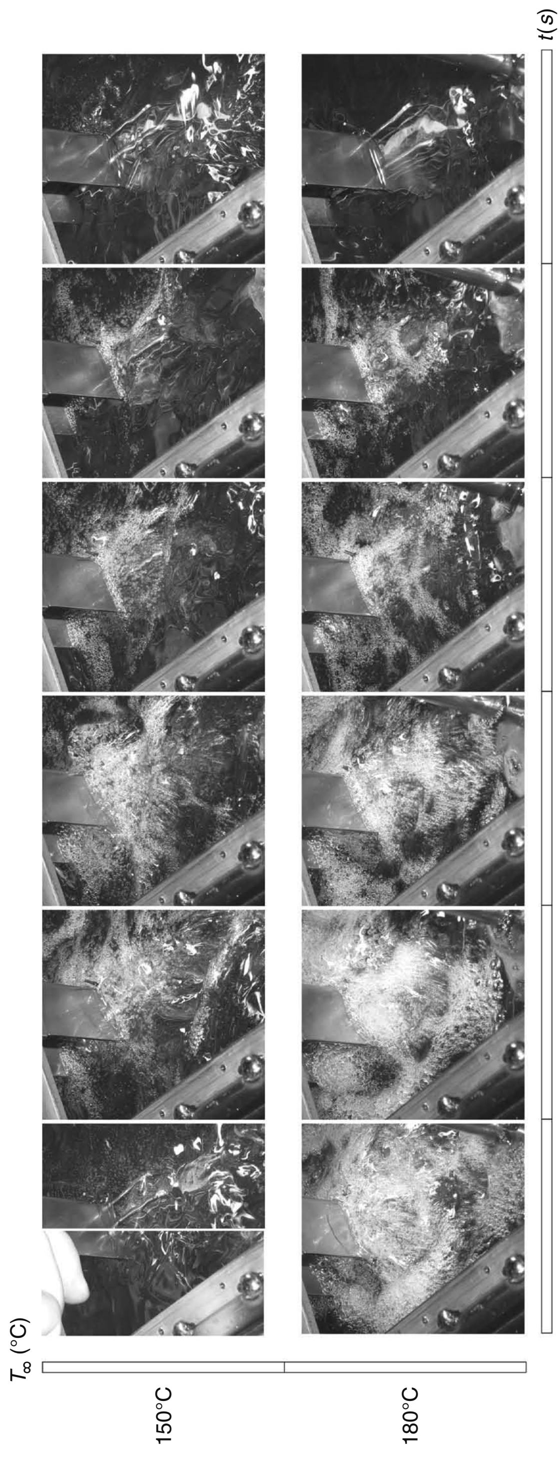



**FIGURE 2.2** Steam bubbles escaping from an immersed alginate gel material into hot oil at 150°C and 180°C. The details of experimental conditions are described in Vitrac, Raoult-Wack, and Trystram (1999).

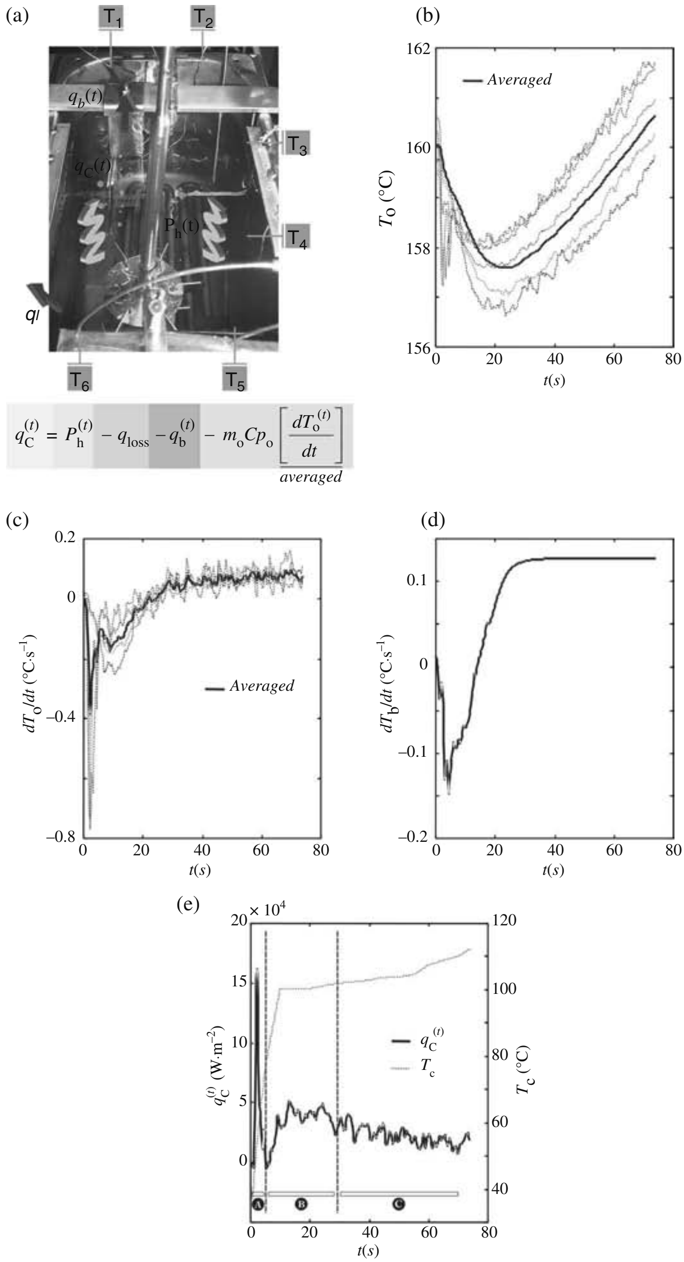



**FIGURE 2.3** Measurement of convective heat flux during batch deep-frying of cassava slices at 160°C: (a) Heat balance: $P_h$, power of heating; $q_{loss}$, heat loss; $q_b$, heat absorbed by the wired baskets used to immerse the product vertically, $m_O$, mass of oil; $Cp_O$ heat capacity of oil; $T_O$, temperature of oil; $q_C$ convective heat flux absorbed by the material; (b) typical oil temperature drop during frying; (c) time derivatives of temperature measurements; (d) rate of heating related to baskets; (e) convective heat flux, $q_C$ and temperature at the geometric center $T_C$. The three identified regimes of heat convection are denoted by A, B and C.

The second regime (regime B) corresponds to an almost constant heat flux between 40 kW·m$^{-2}$ and 50 kW·m$^{-2}$ and a core temperature close to $T_{sat}$. During regime 2, water is vaporized inside the product. An inverse conduction model demonstrated that drying occurred at a vaporization front, which remained located close to exchange surface (Vitrac, Trystram, and Raoult-Wack 2003) and preserved the product surface to heat far from $T_{sat}$.

The third regime (regime C) coincides with an increase of the core temperature above $T_{sat}$ and a decreasing flux.

### 2.2.2 Convective Heat Transfer Coefficient

High convective heat fluxes measured during frying are the consequence of large temperature differences and high conductances between oil and the fried product. In particular, the ejection of steam bubbles at high velocity is expected to be responsible for a significant stirring close to exchange surface (Figure 2.2 and Figure 2.4e–f). Convective heat transfer coefficients ($h$) have been measured with a patented miniaturized active probe (5 mm×5 mm×1.1 mm) (Raoult-Wack, Trystram, and Vitrac 2000) in a heating film sandwiched between two flux-meters and including several thermocouple junctions at the surfaces. Combined with a controlled electrical supply, the whole system enables assessment of the heating of the surface in response to given heating signals. By alternating successive heating signals and cooling periods (without heating), an inverse conduction model gives $h$ at frequency up to 1 Hz with a surface heating $< 3$°C. The characteristics of measurements are detailed and analyzed in Vitrac and Trystram (2005). The configuration used to assess these features in a modified household deep fryer are depicted in Figure 2.4. The $h$ values were measured during frying at different distances from the product surface. It was therefore possible to reconstruct the distribution in time and in space of $h$ values.

The typical variations of $h$ with time, position and bubbling rate are plotted in Figure 2.5 for a model fried food. The model food was a 5 – mm thick slice of alginate gel with a high water content of 13.2 kg of water per kg of dried matter (noted kg·kg$^{-1}$S). The results showed very high initial $h$ values up to 1500 W·m$^{-2}$·K$^{-1}$, which decreased rapidly down to 450 W·m$^{-2}$·K$^{-1}$. The decrease down to the values measured in the bulk flow between 300 W·m$^{-2}$·K$^{-1}$and 350 W·m$^{-2}$·K$^{-1}$ was progressive. The range of maximum values was comparable with those derived from an estimation of the convective heat flux (e.g., from the vaporization rate) and an estimation of the surface temperature (Costa et al. 1999; Hubbard and Farkas 1999; Sahin, Sastry, and Bayindirli 1999; Seruga and Budzaki 2005; Vitrac et al. 2002). The experiments demonstrated that $h$ values were not significantly modified by stirring, and that they were mainly connected to the bubbling at the product surface.

## 2.3 COUPLED HEAT AND MASS TRANSFER INSIDE THE PRODUCT DURING FRYING

Convective heat transfer from oil to the product is responsible for a temperature increase in the product and for an internal vaporization of water. This section details

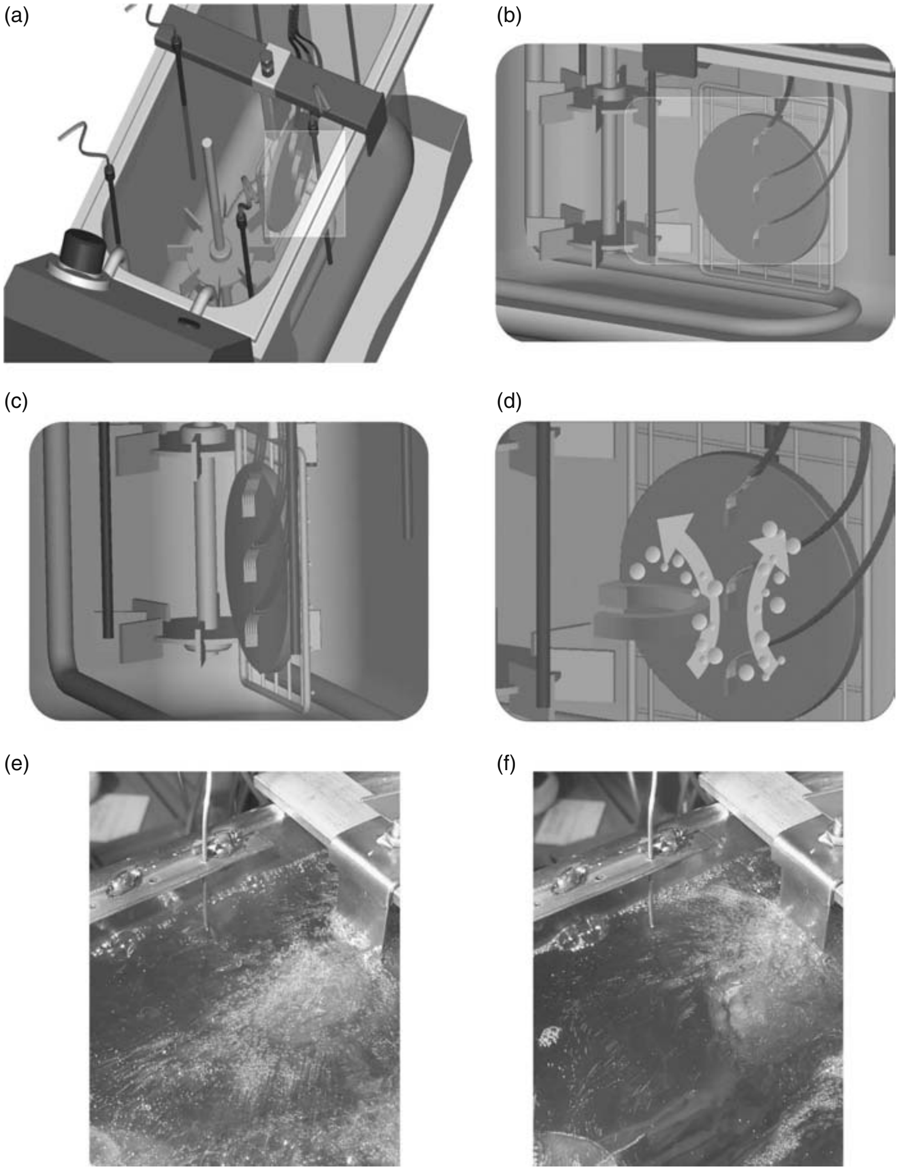



**FIGURE 2.4** Experimental configuration used to assess the distribution of convective heat transfer coefficients during frying: (a–c) Overview of the experimental deep fryer. Three *h*-probes are visible on the different views; (d) Oil flow due to bubbling and mechanical stirring; (e–f) top view of the bubbling flow after (e) 20 s and (f) 200 s of frying at 180°C. (From Vitrac, O., and Trystram, G., *Chemical Engineering Science*, 60. A method for time and spatially resolved measurement of convective heat transfer coefficient (h) in complex flows, 1219–1236, copyright (2005), with permission from Elsevier.)

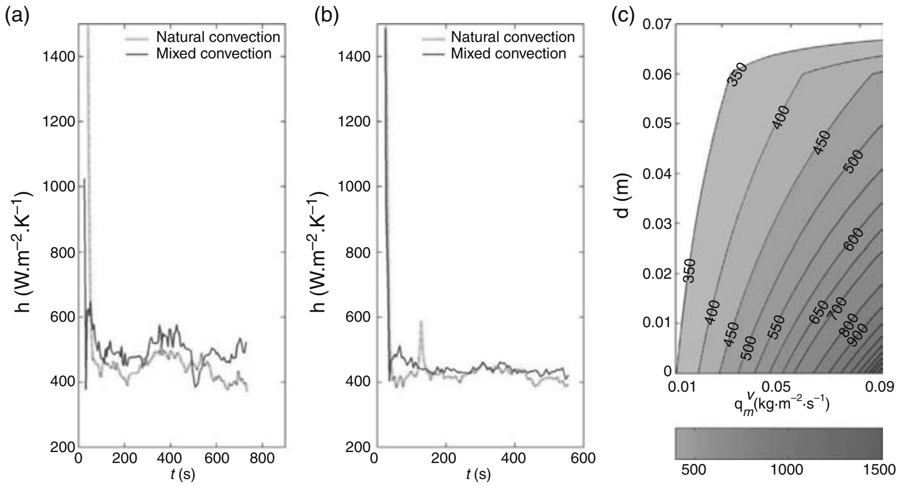



**FIGURE 2.5** Variation of the convective heat transfer coefficient, h, near the product during frying of model gels at: (a) 140°C; (b) 180°C in natural and mixed convection; and (c) Variation of h values with the distance to the fried product and the mass flow rate of steam, $q_m^v$.

how the temperature profile and profile of residual water are connected inside the product and can explain the drying kinetics. The objective is to demonstrate that similar phenomena occur independently of the geometry (e.g., chips or French fries) or the composition of the product. Only the intensity of transfers and the final residual water content are affected by the geometry and the composition.

### 2.3.1 Temperature and Water Profiles During Frying

The initial superficial vaporization (regime A) and subsequent in-depth vaporization during regime B creates a porous dried region and overheated region (heated above $T_{sat}$), which is generically called "crust". Main organoleptic characteristics (texture, color, aroma) are generated in the crust. During the same period and according to the geometry, the core temperature remains below or close to $T_{sat}$. The core contains free or capillary water, but it remains undifferentiated and soft. The main transformations which occur in this region are starch gelatinization and protein denaturation, and they participate in increasing the digestibility of fried food. French fries are removed from oil during regime C, whereas chips are removed after regime C. A review of identified coupled transport phenomena during frying is discussed in Vitrac, Trystram, and Raoult-Wack (2000), Farkas, Singh, and Rumsey (1996), and Ni and Datta (1999).

A typical temperature profile during regime C is outlined in Figure 2.6. The corresponding water content profiles are illustrated on 20-mm thick model alginate gels fried at 170°C in sunflower oil (Figure 2.7). The saturation (i.e., amount of free or capillary water) was measured by nuclear magnetic resonance imaging (MRI) as detailed in Mariette et al. (1999). The starchy gel had a composition in water and starch (initial water content 2.7 kg·kg$^{-1}$s) intermediate of that between cassava and potatoes. The oily gel simulated oily materials such as avocado with an initial oil

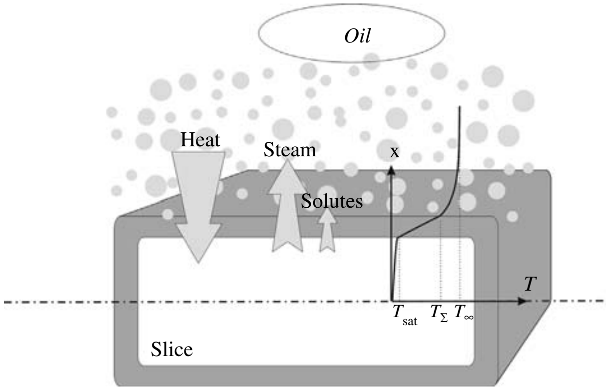



**FIGURE 2.6** Temperature profile in the product during frying.

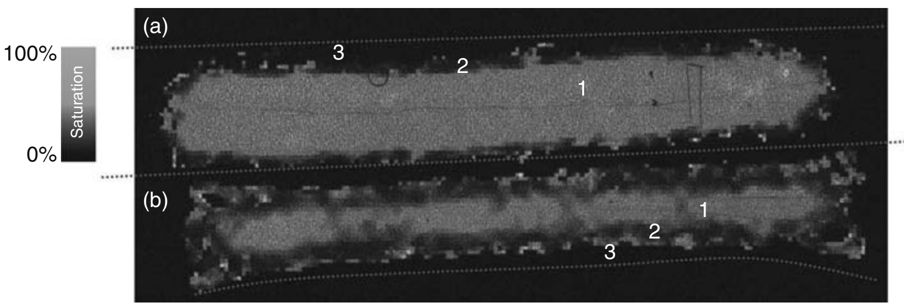



**FIGURE 2.7** Water saturation measured by MRI after frying at 170°C for: (a) a starchy gel (frying time: 10 min); and (b) a oily gel (frying time: 20 min). The initial thickness of slices was 20 mm. The relative amount of removed water is almost similar in both gels (30–40% of initial water was removed): 1—Region with water content close to the initial one; 2—Intermediate region; 3—Hygroscopic region.

content of 22.6% (wet basis) and a water content of 83% (wet basis). The formulation and process of model gel materials are detailed in Vitrac, Raoult-Wack, and Trystram (1999) and in Vitrac, Raoult-Wack, and Trystram (2003).

The starchy gel exhibited a well-identified core region with a composition almost unchanged compared with the initial material. The discontinuity between the core (water saturated region) and the crust (hygroscopic region) is sharp. The transition appears to be more progressive in the oily gel where the intermediate region is larger.

Figure 2.8 and Figure 2.9 show the drying kinetics and temperature kinetics of two typical starchy products: 1.5-mm cassava chips and 5-mm-thick French fries. The corresponding temperature and water content profiles as interpreted with the model that will be described in Section 2.5 for similar products are summarized in Figure 2.10.

As discussed in Section 2.2.1, convective heat transfer during chip frying was classified into three regimes. The three regimes are not discernible on the corresponding experimental drying kinetics of chips (Figure 2.8a) because measurements

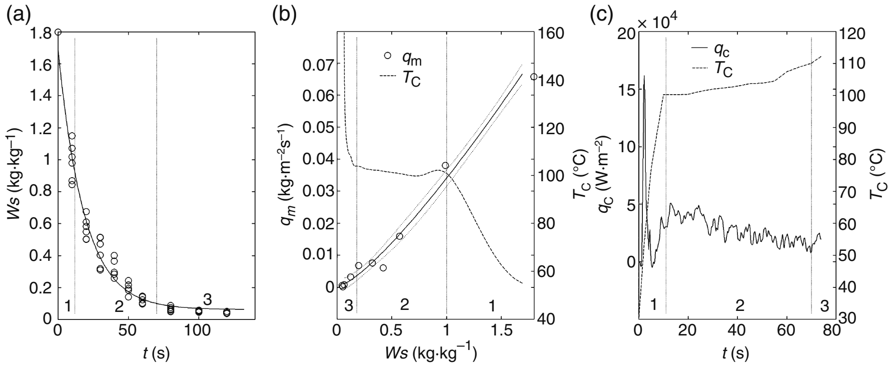



**FIGURE 2.8** Typical drying kinetic of 1.5-mm-thick cassava chips during frying at 160°C in palm oil: (a) variation in residual water content expressed in $kg \cdot kg_S^{-1}$ ($W_S$) with frying time; (b) corresponding drying curve; (c) convective heat flux ($q_C$) and core temperature ($T_C$). (From Vitrac, O., Dufour D., Trystram G., and Raoult-Wack A.L., *Journal of Food Engineering*, 53, Characterization of heat and mass transfer during deep-fat frying and its effect on cassava chip quality, 161–176, copyright (2002), with permission from Elsevier).

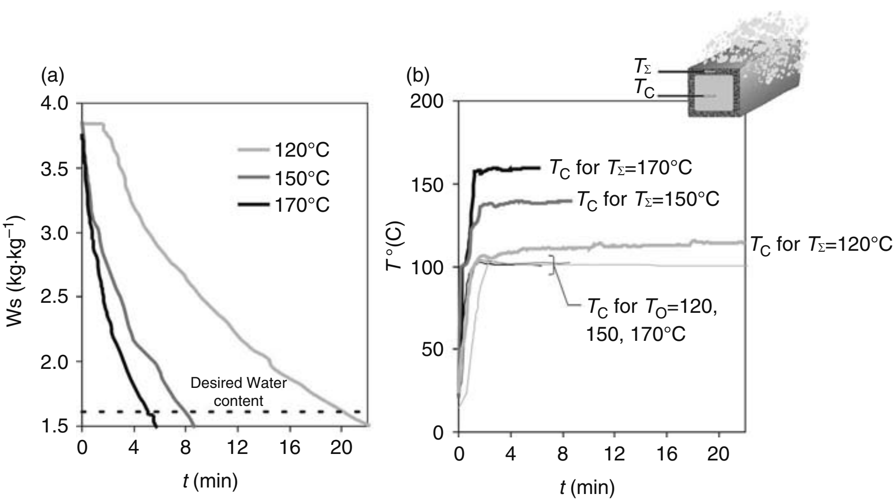



**FIGURE 2.9** Typical: (a) drying and (b) heating kinetics of French fries with geometry 9 mm × 9 mm × 70 mm and initial water content of 3.9 $kg \cdot kg_S^{-1}$ during frying at 120°C, 150°C and 170°C in sunflower oil.

of residual water contents appeared too noisy. As a result, the estimated drying rates, $q_m$ and continuously assessed $q_C$ values looked dissimilar. A more convenient classification of frying stages during chip frying is based not on the dynamics of the surface, but on the dynamics of the core temperature $T_C$. The first stage is defined by $T_C$ below $T_{sat}$ and corresponds almost with the first regime of convective heat transfer related to surface vaporization. The second stage is associated with the situation depicted in Figure 2.6 and $T_C$ values close to $T_{sat}$ values. It gathers consequently regime B and

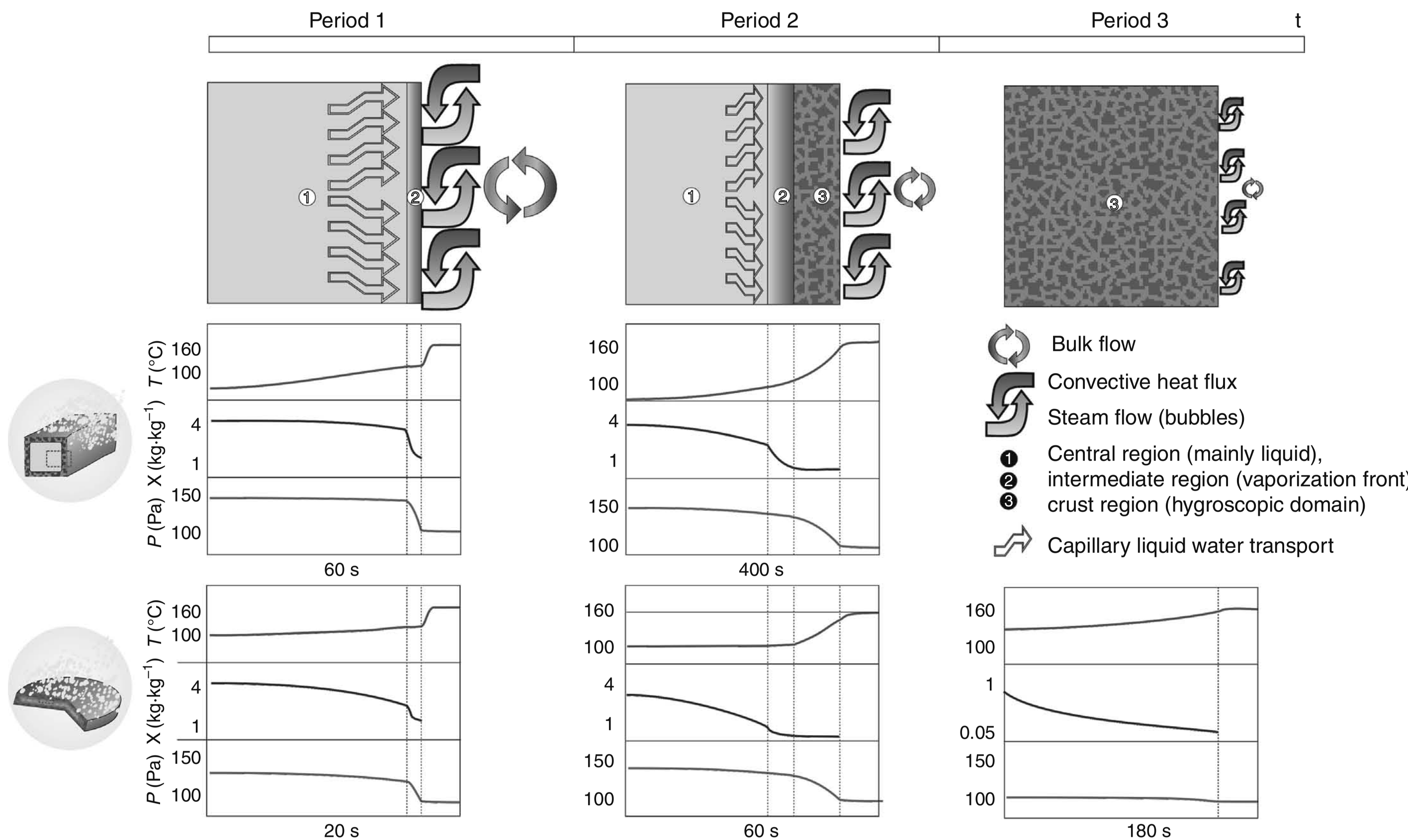



**FIGURE 2.10** Synthesis of simulated temperature and water profiles during frying according to the geometry of the product.

C of convective heat transfer. A detailed analysis of the motions of the vaporization front in Vitrac, Trystram, and Raoult-Wack (2003) showed that stage 2 started with a vaporization front located close to the exchange surface due to an efficient internal liquid water transport (regime B) and was followed by a rapid progression towards the geometric center (regime C). To achieve very low final drying water content in chips and consequently long shelf-lives, chips are fried beyond regime C until the core temperature is significantly above $T_{sat}$. This last and third stage, where the whole product is in the hygroscopic domain (above $T_{sat}$), is associated with low drying rates but rapid heating.

Heat and mass transfer are similar during the frying of thicker products such as French fries and are presented in Figure 2.9. Contrary to chips products, the technological objective is to achieve a final product with an intermediate water content about 55% m/m (wet basis). Accordingly, drying and heating kinetics correspond approximately with those observed during stages 1 and 2 of chips. The first stage of frying at 150°C and 170°C are characterized by a quick heating up to $T_{sat}$ and was associated to a maximum dehydration rate. At 120°C, convective heat transfer at the external surface is limiting, and a significant delay to heating and dehydration is observed. It is highlighted that the evolution of the core temperature, $T_C$, does not depend on the oil temperature, $T_{O,}$ and remains close to $T_{sat}$ as previously noticed by Pravisani and Calvelo (1986). In contrast, the temperature measured close to the exchange surface, $T_{\Sigma}$, is rapidly above $T_{sat}$ and characterizes the heating of the crust in the hygroscopic domain. It is worth noticing that the crust is well-defined at high temperatures ($>$150°C) while it is spread over a larger thickness without showing a sharp transition between the external surface and the core structure at low temperatures (e.g., 120°C).

Figure 2.10 summarizes the temperature and residual water content, $X$ (expressed in $kg{\cdot}kg^{-1}{}_S$), profiles during stages 1 to 3 of frying of typical products such as French fries and potato chips. Heat and mass transfer were simulated in 2D for French fries and potato chips products, the geometries of which were idealized as a square rod of section 5 mm × 5 mm and as a 2 mm thick cylindrical slab of diameter 40 mm, respectively (Vitrac 2000). Similar results are derived from different models (Farkas, Singh, and Rumsey 1996; Ni and Datta 1999; Vitrac, Trystram, and Raoult-Wack 2000; Vitrac et al. 2001). They are used as illustrations of phenomena, which are directly assessible during the same experiment (e.g., Figure 2.8). According to simulated profiles, both materials with different geometries exhibit a similar behavior during the first two periods. The high drying rates generate a flow of steam, which escape the material according to pressure drop from the geometrical center towards the external surface. When the porosity of the material is low, the increase in pressure can significantly change the boiling point of water and reduce the drying rate. For dense materials (e.g., starchy materials with a rigid crust), there is a feedback between the heat transfer, which generates steam, and pressure, which is the driving force for the flow of steam. While the solid matrix is rubbery, the pressure can puff the product. For thin products like chips, heat and mass transfer are more intense and final dehydration during stage 3 is obtained in the hygroscopic domain. For thick products, drying is stopped before stage 3.

Two physical phenomena are particularly highlighted and discussed separately in the following sections:

- a thermodynamical interpretation of the relationship between the local temperature and the local water content in the hygroscopic domain
- the possible internal liquid water transport inside the core region due to a total pressure gradient during the beginning of stage 2 (regime B).

Both phenomena control the position of the vaporization front and affect the thermal history of the product.

### 2.3.2 Thermodynamical Control of Drying in the Hygroscopic Domain

Because the partial pressure of steam during frying is the total pressure, drying is possible only when the product is at or above the boiling point of water. Indeed, it is conventionally assumed that the initial fraction of air is expelled as soon as internal vaporization starts. In first approximation, the boiling point of water in a food product would be the boiling temperature of free water at a similar pressure. In practice, the boiling point of water inside the product is higher as a result of the osmotic pressure generated by solutes and the interactions with solid matrix, which both decrease the vapor pressure in equilibrium. Experimentally, it has been shown that residual water remains in the fried product even when the product is at the thermal equilibrium with oil (no further vaporization rate). The corresponding residual water content increases with the external pressure and decreases with oil temperature. In thin products such as chips, it has been demonstrated that the core temperature versus the residual water content as measured during a frying trial follows approximately the theoretical boiling curve, which governs the thermodynamical equilibrium between adsorbed water and steam (Vitrac et al., 2002). The fried product behaves as it was at each time at thermal equilibrium with a hypothetical bath with a temperature similar to the measured one. This condition is known as local thermodynamical equilibrium and is interpreted because all phases (solid phase, liquid water and steam) are at each time in thermal, mechanical and chemical equilibrium so that the variations of water content and temperature cannot be assumed to be independent. If the total pressure remains uniform and equal to the external pressure during frying (assumption valid for thin or highly porous products), the liquid water–steam equilibrium depends only on a free parameter: either the local temperature or the residual water content expressed respectively to a solid mass frame.

The curve describing evolution of the water content versus the temperature at a given pressure is called the boiling curve or desorption isobar. Typical isobars at 100 kPa for starchy and oily products are plotted in Figure 2.11 and their consequences on the local product thermal history are illustrated in Figure 2.12. Because the water content is related to the non-fat solid content, the isobar can be determined at thermal equilibrium during successive frying experiments, or equivalently during successive drying experiments in superheated steam. It is worth noticing that either the oil content or the thermo-mechanical history of the product does not significantly modify the isobars because they characterize the specific physicochemical interactions between water and the solid matrix. The interaction energy is expressed as an equivalent boiling temperature, which corresponds to the required kinetic energy to stop these interactions. It is expected that the effect of pressure on the boiling point of

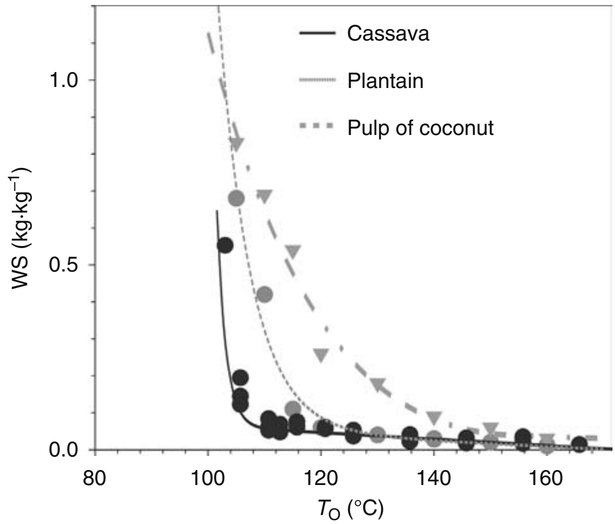



**FIGURE 2.11** Equilibrium curves for different starchy (cassava, plantain) and oily products (pulp of coconut) obtained for different frying temperatures $T_O$.

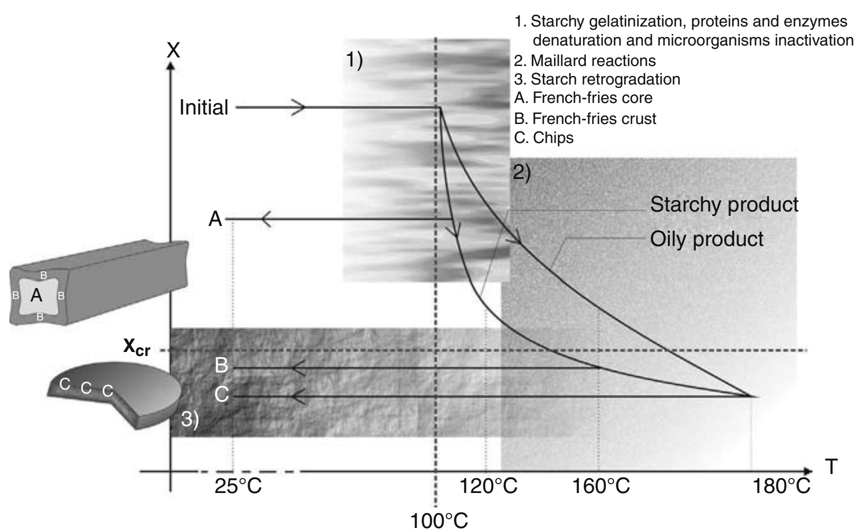



**FIGURE 2.12** State diagram of the hydrothermal history and of related product transformations for different geometries and product compositions.

water is higher for free and capillary water than for dispersed water in strong interactions with the solid matrix (sorption due to electrostatic interactions, intermingling with a polymer phase).

Below the boiling point of free water, the local temperature does not depend on the water content. At a temperature slightly above the boiling point of water, the water content decreases sharply. This stage corresponds to the vaporization of water which interacts weakly with the solid matrix: capillary water and cell content. Its temperature

is close to the temperature of free water. At higher temperatures, the variation of the residual water content with temperature is lower, and asymptotic behavior is observed. The isobar shape varies significantly with the composition and the cohesive energy of the solid matrix. For instance, model alginate gels with very high water content ($>92\%$ m/m) exhibit a very sharp decrease in the final water content that is almost independent of the temperature In contrast, oily materials such as coconut, avocado and meat products present a slower decrease in water content spread over a wider range of temperatures. These descriptions are consistent with experimental observations during frying: the drying of materials such as gels is much faster than oily/fatty products. The drying rate of starchy products is intermediate.

### 2.3.3 Internal Liquid Water Transport During Frying

Several experimental results have demonstrated that liquid water transport has a significant role during frying. It is responsible for cooling of the product surface during regime B (beginning of stage 2) and preserves the product from rapid overheating and darkening (Vitrac et al. 2002; Vitrac, Trystram, and Raoult-Wack 2003). A wireless autonomous temperature–pressure logger model inserted in a starchy gel demonstrated that the driving force of liquid water transport was a total pressure gradient (Vitrac, Trystram, and Raoult-Wack 2000). For materials with weak structure due to high water content and/or due to the absence of cell structure (e.g., apples), liquid water transport can be so intense that liquid water escapes the product surface without vaporization (Vitrac, Raoult-Wack, and Trystram 2003; Vitrac and Bohuon 2004).

A direct estimation of liquid mass flow rate during frying was done using a special experiment in which an instrumented micro-channel was created in a model gel, as detailed in the study of Vitrac (2000). Channel walls comprised a heating film and two flux-meters (Figure 2.13). The experiment starts by heating the gel in

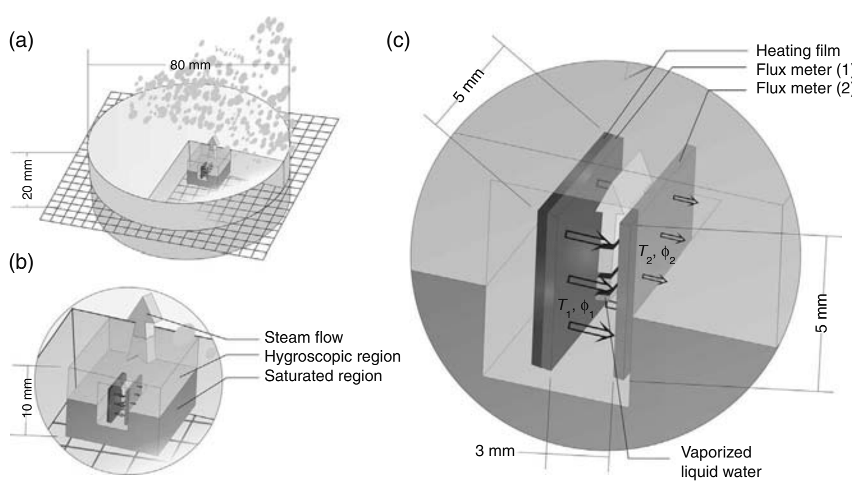



**FIGURE 2.13** Principle of liquid water flux measurement inside a model gel material: (a) Slice molten around a micro-flow meter; (b) Interpretation of flow through the channel; (c) Detail of the instrumented vaporization channel.

boiling water prior to frying at 180°C. The surface of the channel is maintained at a temperature between 115°C and 120°C during frying so that the channel cannot contain any liquid or capillary water. The amount of liquid water crossing the channel is proportional to:

$$q_{\mathrm{m}}^{1} = \frac{S}{C}\frac{\phi_1 - \phi_2}{\Delta H_v} \tag{2.1}$$

where $\{\phi_i\}_{i=1,2}$ are the measured flux densities in $W{\cdot}m^{-2}$, $S$ is the surface area of the flux meter, and $C$ is cross-sectional surface area.

A typical result is presented in Figure 2.14. An almost insignificant liquid water flux is observed while the vaporization front does not cross the channel. At this stage, the measured liquid flux is maximal, with a liquid mass flow rate up to 0.01 $kg{\cdot}m^{-2}s^{-1}$ and is progressively decreasing.

## 2.4 OIL UPTAKE DURING COOLING

### 2.4.1 Oil Profile inside the Product

#### 2.4.1.1 At the Macroscopic Scale

The previous description of heat and mass transfer did not cover oil uptake. Oil repartition inside the product after frying can be observed using dyed oil as the frying medium (Keller, Escher, and Solms 1986; Ufheil and Esher 1996). Figure 2.15 presents, at different scales, cross-sections of French fries obtained after frying at

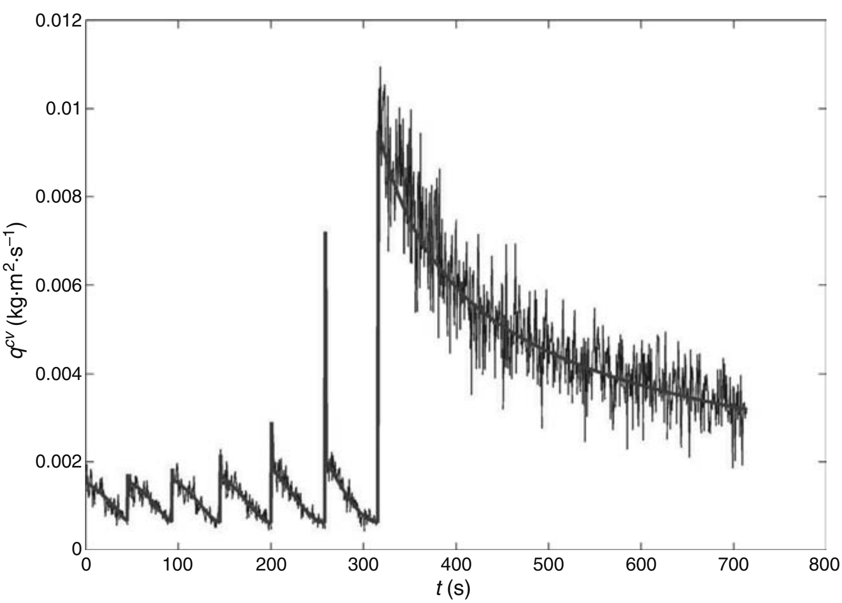



**FIGURE 2.14** Liquid water flux measurements at the level of the sensor presented in Figure 2.12 during frying at 180°C.

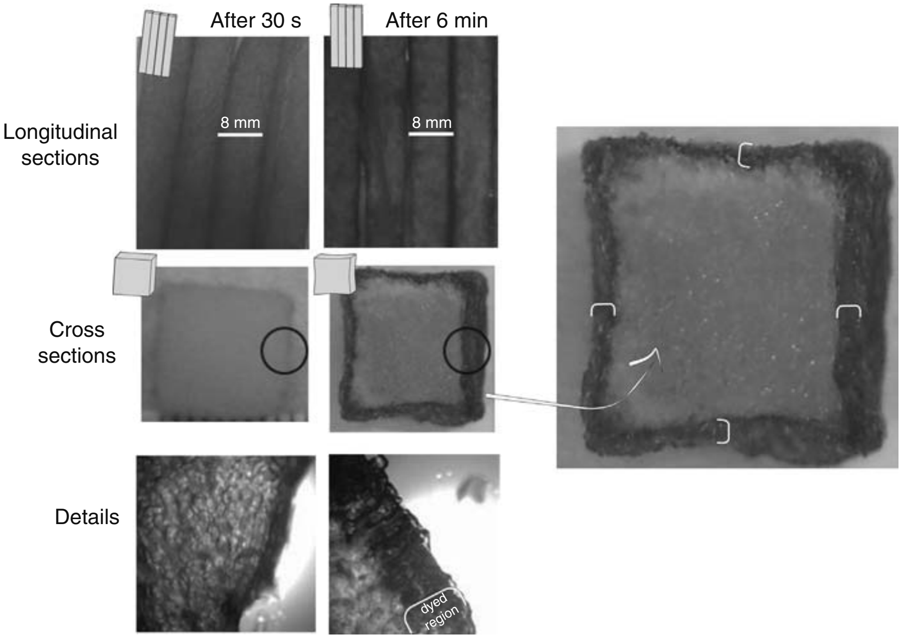



**FIGURE 2.15** Distribution of oil uptake in French fries after 30 s and 6 min of frying at 170°C in sunflower oil dyed with Sudan Red.

170°C in oil dyed with Sudan red. For short frying times (30 s), oil is nearly invisible inside the product. The crust appears completely colored in final French fries (i.e., after 6 min of frying) but is not detected in the core region. Microscopic observations of the crust show that oil fills the voids freed by the vaporized water. Oil tends to replace water inside the product because the shrinkage of the product during frying is incomplete.

### 2.4.1.2 At the Scale of Cell Structure

Oil uptake at the scale of the microstructure can be observed after frying in three dimensions using confocal laser scanning microscopy (CLSM). Compared with other techniques based on cryofractures, the main interest of this method is that cross-sections are non-intrusive and are done by moving the confocal plane inside the product. Oil uptake is visualized by dying the frying oil with a thermostable fluorescent probe. Figure 2.16 presents a three-dimensional (3D) reconstruction of oil uptake in the first cell layer (total thickness, 150 μm) of the crust in CLSM, where the cell walls are simultaneously observed using their natural fluorescence when they are excited with a continuous-wave UV laser (351 nm). In this particular experiment, a French fry was laid down on a cover slip covered with a thin film of dyed oil.

As described by Pedreschi and Aguilera (2002), oil uptake appeared to wrap the surface of parenchyma cells of potato like an “egg-box.” Nevertheless, current observations show that oil preferably fills the cells damaged by the initial cutting and penetrates the structure between dislocated and fractured cells. The corresponding percolation network is mainly created by the propagation of disruptions induced by

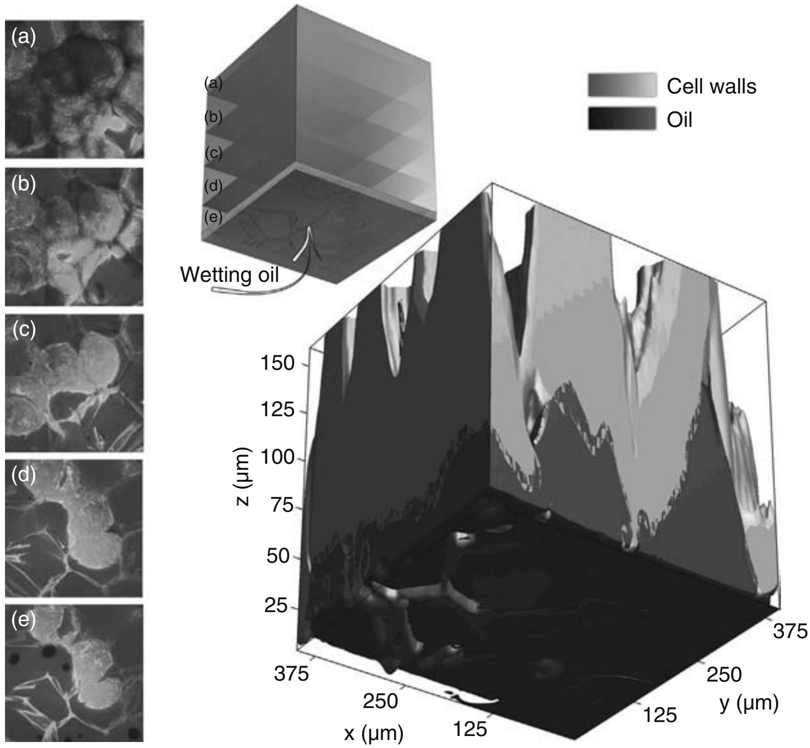



**FIGURE 2.16** Three-dimensional reconstruction of oil distribution and cell walls during cooling at thermal equilibrium with UV-VIS confocal laser scanning microscopy. The cell walls are visualized in light gray and oil uptake in dark gray.

the initial cutting in the direction normal to the exchange surface. The mechanical forces responsible of the structure deformations and possibly ruptures are the friction losses created by steam escaping the product. Cells filled with gelatinized starch appear less impregnated even if they are damaged.

### 2.4.2 Mechanisms of Oil Uptake

Several authors using dyed or labeled oil (Ufheil and Esher 1996; Saguy et al. 1997) or using successive washings with solvent (Moreira, Sun, and Chen 1997) demonstrated that oil uptake occurs mainly during cooling immediately after frying. Vitrac, Trystram, and Raoult-Wack (2000) confirmed these observations by measuring the internal pressure within a model starch material during frying and cooling. An overpressure of 45 kPa was assessed during frying and prevented any migration of oil inside the material. In contrast, rapid cooling of the crust in the hygroscopic domain after frying generated an immediate condensation of steam in equilibrium with the solid matrix (i.e., following the sorption isobar described in Figure 2.11) and was responsible for a pressure drop down to 35 kPa. Repetitions for materials with different composition and structure demonstrated that pressure values depended on the apparent density and porosity of the material.

Figure 2.17 summarized the identified phenomena that control oil uptake during cooling. As detailed by Gamble and Rice (1987) and Moreira and Barrufet (1996), oil sticks to the surface when the product is removed from oil and fills the accessible voids in competition with air. As a result, only products which are sufficiently dried at their surface can be wetted and impregnated with oil. The main driving forces are the capillary pressure and the possible pressure drop generated by steam condensation. The resistances to oil migration are related to oil viscosity, and to the connectivity of voids freed by the removed water or created by cell dislocations. As a result, significant differences in oil uptake pattern can be obtained with different oils or different product structures.

A simplified description of oil uptake of the scale of a pore created by the escape of water is reproduced on Figure 2.18. If the food material was cooled submerged in oil, oil would fill all voids, which were accessible from its external surface. If the food material was cooled in air and in a non-limiting reservoir of oil at the external surface, the maximum capillary rise, noted $z_{max}$, in a vertical pore would correspond to the Jurin's height, which defines a mechanical equilibrium between the capillary force and the weight of liquid column. For a horizontal pore, it would correspond to complete filling of accessible voids. This description is not consistent with the observation because oil is drained and dripped during the cooling stage so that the film of oil which surrounds the product is limiting. Because the mechanical equilibrium cannot be reached, the maximum oil ascension is lower than $z_{max}$ and is governed by the dynamic balance of forces acting of the liquid column of mass $m_O$ and with an averaged velocity $v_O$:

$$\underbrace{\frac{d}{dt}\left[m_O^{(t)} \cdot v_O^{(t)}\right]}_{\text{momemtum variation}} = \underbrace{2 \cdot \pi \cdot r \cdot \gamma \cdot \cos\theta}_{\text{capillary force}} \underbrace{- 8 \cdot \pi \cdot \mu_O \cdot v_O \cdot z}_{\text{viscous force}} \underbrace{- \pi \cdot r^2 \cdot z \cdot \rho_O \cdot g}_{\text{weight}} \tag{2.2}$$

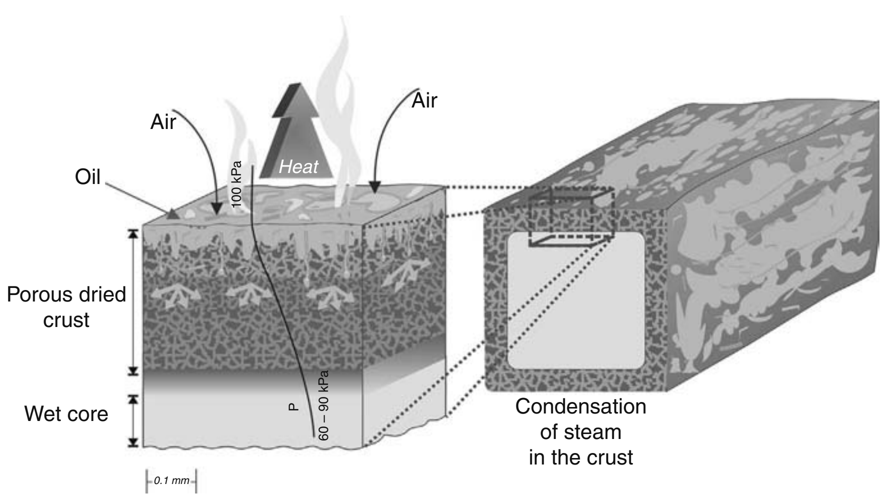



**FIGURE 2.17** Physical interpretation of oil uptake during cooling.

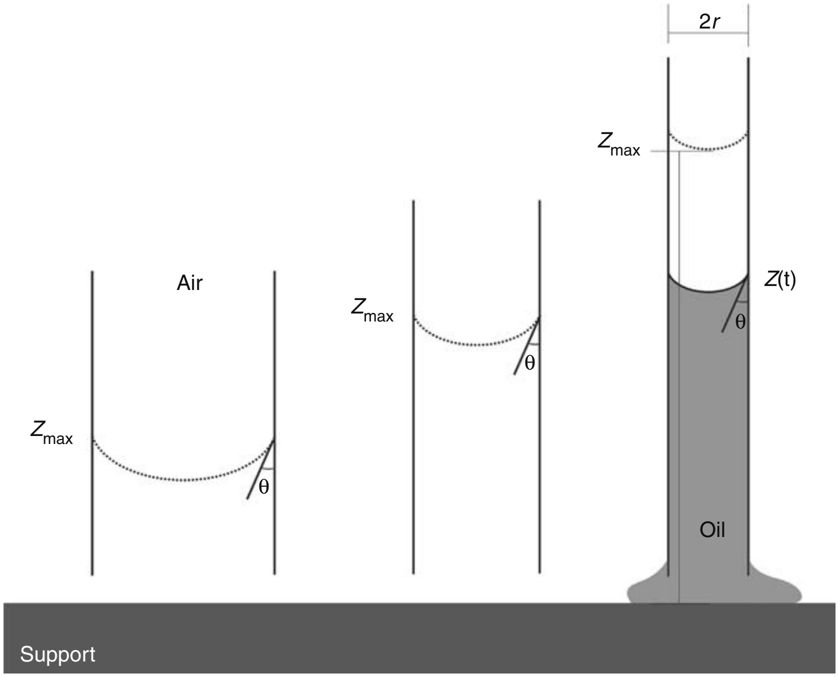



**FIGURE 2.18** Simplified description of oil uptake though vertical capillary tubes of different diameters. The dashed meniscus represents the Jurin's height (i.e., maximum height that can be theoretically reached at mechanical equilibrium). The meniscus in continuous line represents the position of the oil uptake front out of equilibrium.

where $\gamma$ is the interfacial tension between the oil and air, $\theta$, is the wetting angle between oil and the solid, $\mu_O$, and $\mu_O$ are the oil viscosity and density, respectively.

$z_{max}$ is inferred from Equation 2.2 at equilibrium, i.e., when the velocity and the variation of momentum vanish:

$$z_{max} = \frac{2 \cdot \gamma \cdot \cos\theta}{\rho_O \cdot g \cdot r} \tag{2.3}$$

As a result, it is worth noticing that the capillary rise varies as the reciprocal of the pore radius, while the amount of oil uptake $m_O^{eq} = \rho \cdot \pi \cdot r^2 \cdot z_{max}$ is proportional to the $r$. In other words, oil uptake at equilibrium is expected to be higher when the pores are larger, but oil impregnation is expected to be deeper when the pores are smaller. Moreira, Palau, and Xiuzhi (1995) found that decreasing pore radius from 20–2 μm increased the final oil content of tortilla chips by 15%. The main deviations are assumed to be related to the deviation from the equilibrium and to the connectivity of pores. In contrast with the equilibrium relationship (Equation 2.3), the dynamic equation (Equation 2.2) introduces an additional force, which opposes the penetration of oil: viscous forces. The role of viscous forces is observed by comparing the oil uptake of chips fried in palm oil (melting point about 30°C) and cotton seed oil (melting point about

7°C). Palm oil, which solidifies rapidly during cooling, leads to a high surface adhesion and a low penetration depth, whereas cotton seed oil penetrates deeply inside the product (Vitrac et al. 2002). Because ageing increases oil viscosity (Tseng, Moreira, and Sun 1996), large discrepancies in oil uptake between processes are expected.

More sophisticated descriptions of oil percolation have been proposed in the literature (Moreira and Barrufet, 1998; Bouchon and Pyle 2005). In particular, Bouchon and Pyle (2005) took into account the condensation of steam as an additional driving force.

## 2.5 SIMPLIFIED FRYING MODEL WITH ONE TRANSPORT EQUATION

The main complication in the modeling of coupled heat and mass transfer arises from the difficulty in predicting the location of the region subjected to a change of state (freezing/thawing, drying/condensation, frying) and the corresponding rate of change. Because heat is transferred from the external surface, the system can always be decomposed into a region in contact with the exchange surface (which has already undergone a change of state) and a core region (which still contains liquid water). Both regions would be separated by a moving boundary (Farkas, Singh, and Rumsey 1996). This description, known as the "Stefan problem," is not completely realistic during frying because it would predict that the drying would stop as soon as the temperature at the geometrical center is above the boiling point of water, which is not verified experimentally. An alternative is to envision that vaporization occurs in all regions above the starting boiling point of water according to the desorption isobar $X=\beta(T)$. Following the principle of local thermodynamical equilibrium, the local rate of vaporization at a given temperature (above the starting boiling point) is proportional to the elemental variation of the water content with temperature (Figure 2.11) written as:

$$f=\varepsilon_s\cdot\rho_s\cdot\Delta H_\text{v}\cdot\left.\frac{\partial X}{\partial t}\right|_T=\varepsilon_s\cdot\rho_s\cdot\Delta H_\text{v}\cdot\left.\frac{\partial X}{\partial T}\right|_T\left.\frac{\partial T}{\partial t}\right| \tag{2.4}$$

where $\rho_s$ is the intrinsic density of the solid matrix, and $\varepsilon_s$ is the apparent porosity of the solid matrix. The latter is assumed to be constant in this model (no shrinkage or expansion). $X$ is the local mass concentration in water expressed in kg·kg$^{-1}$ of solid matrix. $\Delta H_\text{v}$ is the latent heat of vaporization, which may vary with the water content if the isosteric heat of desorption is included.

A general transport equation using the temperature as state variable and taking into account the vaporization is obtained by introducing Equation 2.4 as a source term within a conduction equation in an Eulerian reference frame:

$$\overline{\rho_s}\cdot\left(\overline{Cp}^{(T)}-\Delta H_v\cdot\left.\frac{\partial X}{\partial T}\right|_T\right)\cdot\frac{\partial T}{\partial t}=\nabla\cdot\left(k^{(\beta(T))}\cdot\nabla T\right) \tag{2.5}$$

where $\overline{Cp}^{(T)}$ is the apparent heat capacity of the system and defined by a mixture rule of the three heat capacities $\left\{Cp_i^{(T)}\right\}_{i=s,l,v}$ with $s=$ solid, $l=$ liquid water and $v=$ steam:

$$\overline{Cp}^{(T)} = Cp_s^{(T)} + X \cdot Cp_l^{(T)} + \left(X_0 - X\right) \cdot \frac{\rho_v}{\rho_l} \cdot Cp_v^{(T)}$$
$$= Cp_s^{(T)} + \beta\left(T\right) \cdot Cp_l^{(T)} + \left[X_0 - \beta\left(T\right)\right] \cdot \frac{\rho_v}{\rho_l} \cdot Cp_v^{(T)} \tag{2.6}$$

$k(\beta(T))$ is the equivalent thermal conductivity of the mixture, which is assumed to decrease significantly with water content given by: $X=\beta(\mathrm{T})$.

At the oil–product interface, noted $\partial\Omega$, a generalized Neumann boundary condition taking into account the transport of heat by convection on the oil side is assumed (Vitrac, Raoult-Wack, and Trystram 2003):

$$-k^{(\beta(T))} \cdot \nabla T \cdot \vec{n}\Big|_{\partial\Omega} = h^{(q_v)} \cdot \left(T\Big|_{\partial\Omega} - T_O^{(T)}\right) \tag{2.7}$$

where $\vec{n}$ is the normal vector, and $T_O^{(t)}$ is the oil temperature (which may vary with time in household or industrial devices). $h^{(q_m^v)}$ is the convective heat transfer coefficient, which may vary with the vaporization rate, noted $q_m^v$.

At the axis of symmetry or symmetry planes, noted $\partial\Omega_0$, an insulation boundary condition is assumed:

$$\nabla T \cdot \vec{n}\Big|_{\partial\Omega_0} = 0 \tag{2.8}$$

It is worth noticing that the current description neglects the oil uptake and its effect on heat transfer.

The main assumptions to simulate coupled heat and mass transfer during frying of a product similar to cassava chips are presented in Figure 2.19. Simulated results corresponding to experimental conditions detailed in Figure 2.3 and Figure 2.19 are plotted in Figure 2.20. Compared with the experimental drying kinetic, the predicted one is slightly slower due to an absence of an internal liquid transport in product, as discussed in Vitrac, Trystram, and Raoult-Wack (2003). Indeed progression of the moving vaporization front is too fast, and the increase of heat transfer resistance created by the crust is consequently overestimated. The main features of coupled heat and mass transfer are preserved. In particular, the heating of the material in the hygroscopic domain is appropriately described. It is emphasized that the initial peak in temperature at the product surface (Figure 2.20b) is related to the intensification of convective heat transfer at the beginning of frying, which decreases sharply during regime B.

## 2.6 CONCLUSIONS

During the past 20 years, most of heat and mass phenomena occurring during or immediately after deep-fat frying have been elucidated. The latest progress in understanding is summarized in Table 2.1. One of the most significant contributions was to confirm that oil could not penetrate the food product, while an overpressure exists inside the product. As a result, it was possible to separate the description of heat and

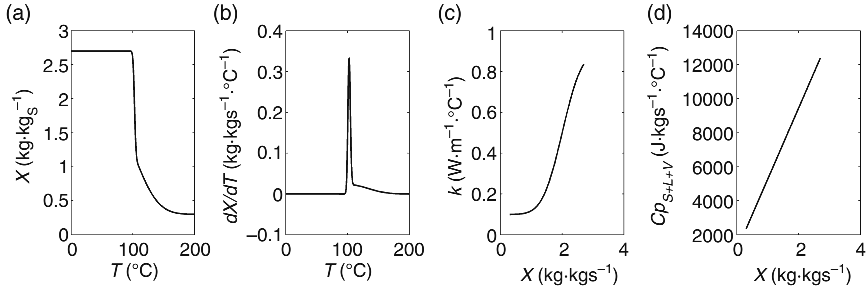



**FIGURE 2.19** Main physical properties required to simulate the frying process: (a) desorption isobar; (b) its derivative with temperature; (c) apparent thermal conductivity; (d) apparent heat capacity.

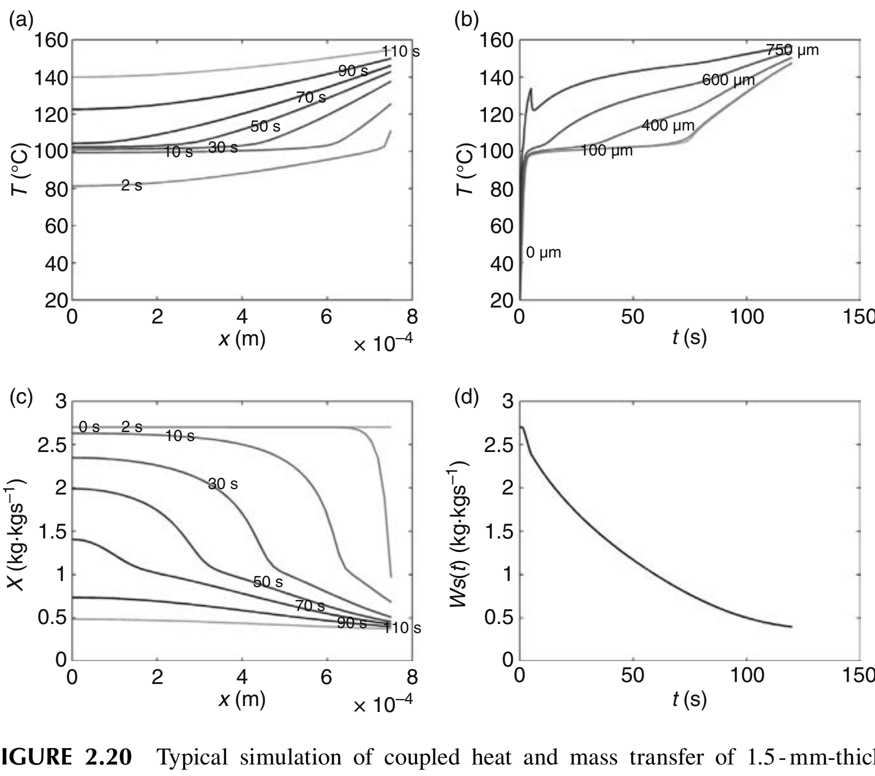



**FIGURE 2.20** Typical simulation of coupled heat and mass transfer of 1.5-mm-thick cassava chips fried during 120 s at 160°C (input data are plotted in Figure 2.8): (a) temperature profiles; (b) temperature kinetics; (c) water content profiles; (d) residual water content kinetics.

mass transfer during frying (i.e., in the absence of an incondensable phase: air and in the absence of oil inside the product) and during cooling (i.e., in the presence of oil and of an incondensable phase: air). As a result, the temperature inside the product during frying follows the isobar of desorption of water. Similarly, the condensation of water inside the product during cooling can occur at a temperature above the

**TABLE 2.1**
**Synthesis of Significant Heat and Mass Transfer Phenomena Occurring during the Frying Process for Thin and Thick Products**

| | | During Frying | | During Cooling | | |
|---|---|---|---|---|---|---|
| **Physical Phenomena** | **Interpretation** | **Thin Products** | **Thick Products** | **Thin Products** | **Thick Products** | **Ref.** |
| External heat transfer | Convection with oil | 750 $W.m^{-2}.K^{-1}$ | 650 $W.m^{-2}.K^{-1}$ | | | (1–2) |
| | Convection | | | 51 $W.m^{-2}.K^{-1}$ | 51 $W.m^{-2}.K^{-1}$ | |
| Internal heat transfer | Averaged thermal conductivity | 0.1 $W{\cdot}m^{-1}{\cdot}K^{-1}$ | 0.4 $W{\cdot}m^{-1}{\cdot}K^{-1}$ | | | (3) |
| Internal pressure | Due to pressure drop required for steam escape or due to steam condensation | | 1.1–1.4 bar | | 0.7 bar | (4) |
| Internal mass transfer | Steam flow | +++++ | + | – | – | (1) |
| | Liquid water transport | Observed | Not observed | – | – | (5) |
| | Oil uptake | only at the very end of frying | Not observed | +++ | + | (6) |
| Mechanical modifications | Increase of porosity in the crust (due to voids left by water and internal deformations) | +++ | + | | | (7–8) |
| | Ratio crust/crumb | +++ | + | | | |
| | Puffing due to an overpressure | +++ | + | | | |
| | Shrinkage | +++ | + | +++ | + | |

*Note:* Intensity scale of the phenomenon from very low (–) to very high (++++).
(1) Costa et al. (1999), (2) Moreira and Barrufet (1998), (3) Bouchon and Pyle (2005), (4) Vitrac (2000), (5) Vitrac, Trystram, and Raoult-Wack (2003), (6) Ufheil and Escher (1996), (7) Pinthus, Weinberg, and Saguy (1995), (8) Moreira, Castell-Perez, and Barrufet (1999).

boiling point of free water, and may contribute to oil uptake as soon as the cooling process starts.

It is worth noticing that our current understanding is mainly macroscopic and takes into account only some aspects of the evolution of the food product. Thus, the evolution of the microstructure (e.g., initial cellular structure) and its mechanical properties, as well as the coupling between reactions and heat and mass transfer, are poorly understood. Such knowledge is required to extend the range of fried products for food and non-food applications. The effect of cooling conditions (cooling temperature and pressure, drainage) on the mechanisms of oil uptake are not well characterized, and suggest that significant additional reduction in oil uptake could be still achieved. Models of capillary pressure and permeability of fried food products to oil seem to be particularly desirable.

## NOTATIONS

| | |
|---|---|
| $C$ | cross-sectional surface area ($m^2$) |
| $Cp$ | heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$) |
| $h$ | convective heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$) |
| $\Delta H_v$ | latent heat of vaporization ($J \cdot kg^{-1} \cdot C^{-1}$) |
| $k$ | thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$) |
| $m_O$ | mass of oil column (kg) |
| $P_h$ | heating power (W) |
| $q_m^l$ | liquid mass flow rate ($kg \cdot m^{-2} \cdot s^{-1}$) |
| $q_m^v$ | steam mass flow rate ($kg \cdot m^{-2} \cdot s^{-1}$) |
| $q_C$ | convective heat flux density ($W \cdot m^{-2}$) |
| $r$ | pore radius (m) |
| $S$ | surface area ($m^2$) |
| $t$ | time (s) |
| $T$ | Temperature (°C) |
| $T_{sat}$ | saturation temperature of free water (°C) |
| $v_O$ | velocity of oil column ($m \cdot s^{-1}$) |
| $Ws$ | residual water content in material ($kg \cdot kg^{-1}$ non-fat dry basis) |
| $X$ | local water content ($kg \cdot kg^{-1}$ non-fat dry basis) |
| $z$ | height (m) |
| $\beta$ | desorption isobar |
| $\gamma$ | interfacial tension ($N \cdot m^{-1}$) |
| $\mu$ | viscosity (Pa·s) |
| $\rho$ | density ($kg \cdot m^{-3}$) |
| $\theta$ | contact angle (rad) |
| $\varepsilon$ | apparent density ($kg \cdot m^{-3}$) |
| $\phi$ | heat flux ($W \cdot m^{-2}$) |

### SUBSRIPTS

| | |
|---|---|
| $C$ | core |
| $\Sigma$ | surface |

| | |
|---|---|
| $O$ | oil |
| $v$ | steam |
| $s$ | solid |
| $l$ | liquid |
| $0$ | initial |

### Other Symbol

| | |
|---|---|
| $\partial\Omega$ | oil–product interface |
| $\partial\Omega_0$ | symmetry plane |
| $\vec{n}$ | normal vector |
| $\bar{X}$ | volume average of X |

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# 3 Chemistry of Frying

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## CONTENTS



## 3.1 INTRODUCTION

There has been a great increase in the consumption of frying fats and oils over the last decade. This followed the development of a wide range of new products, most notably frozen prefried foods and "fast foods."

Frying is a rapid and convenient technique for producing palatable and desirable foods with unique characteristics of flavor, color and odor. However, during the frying process, the oil or fat is exposed to high temperature in air and moisture. Under

these conditions, a complex series of reactions takes place, resulting in the loss of quality of the frying oil and of the fried food. Although general modifications of the main fat constituents (oxidation, polymerization and hydrolysis) are well-known, it is not easy to forsee the rate of fat degradation due to many variables involved in the frying process. Some are linked to the process (e.g., temperature, length of heating, continuous or discontinuous heating, turnover rate) to the food (i.e., lipid composition, main and minor constituents) or to the oil or fat (e.g., degree of unsaturation, initial quality and additives).

The new compounds formed differ in polarity from the major compounds initially present in the fresh oil, i.e., the non-altered triglycerides (TGs). This property is the basis of the most important method in the analysis of used frying fats—determination of polar compounds—included in most of the official regulations in different countries. They establish that used frying fats and oils must be rejected for human consumption when the content of the polar compounds is about 25% (Firestone 1996).

This chapter is dedicated to the chemistry of frying, and the contents have been divided into three major sections. The first section covers the main changes taking place in the frying oil, the present analytical techniques applied for the quantification of new compounds formed and their relative importance are considered in the second section; and the last section focuses on the interactions between the food and the frying oil.

## 3.2 CHANGES IN OIL DURING FRYING

Most of the information on oil modifications has been obtained by heating oils at frying temperatures in the absence of food. This approach has the advantages of distinguishing between the formations of new compounds attributable to the frying conditions excluding the food and, in a latter stage, facilitates the definition of the compounds present in the frying medium due to the interaction with the food. In the next sections, the formation of the most important groups of compounds due to the action of oxygen, temperature, and food moisture are discussed separately.

### 3.2.1 Oxidative Reactions

The chemistry of lipid oxidation at the high temperatures of food processes like baking and frying is highly complex because oxidative and thermal reactions are involved simultaneously. As temperature increases, the solubility of oxygen decreases drastically, although all oxidation reactions are accelerated.

Figure 3.1 shows the well-known scheme of the oxidation process. It proceeds via a free-radical mechanism of chain reactions, where RH represents the TG molecule undergoing oxidation in one of its unsaturated fatty acyl groups. At frying temperature, as the oxygen pressure is reduced, the initiation reaction becomes more important and the concentration of alkyl radicals ($R^\bullet$) increases with respect to alkylperoxyl radicals ($ROO^\bullet$). As a result, polymeric compounds are predominantly formed through reactions mainly involving $R^\bullet$ and alkoxyl radicals ($RO^\bullet$) (Scott 1965). These facts are in agreement with the experimental results stated below.

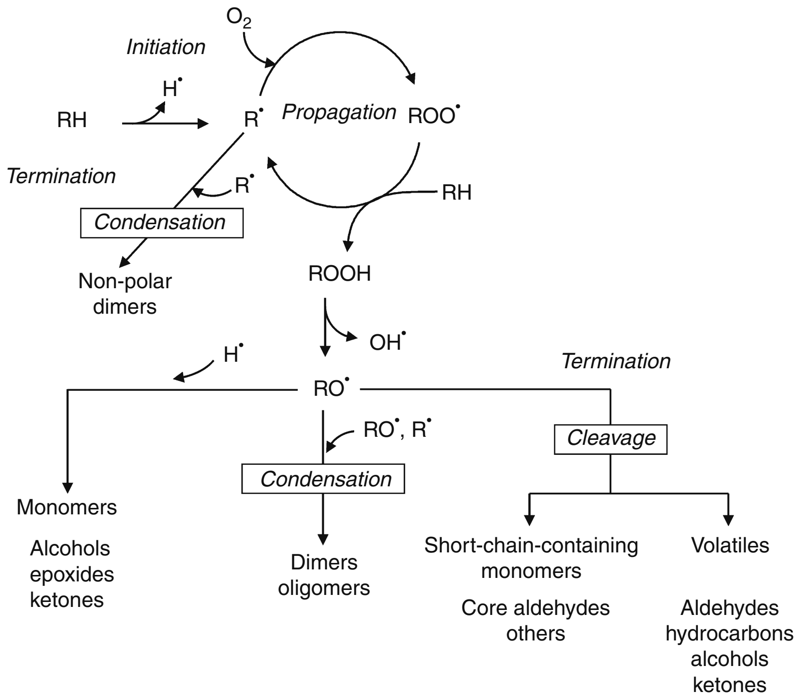



**FIGURE 3.1** Mechanism of thermal oxidation (schematic).

- At low or moderate temperatures, formation of oxidation compounds during the induction period is slow; hydroperoxides (ROOH) are the major compounds formed, and their concentration increases until the advanced stages of oxidation. Polymerization compounds become significant only in the accelerated stage of oxidation after the end of the induction period (Márquez-Ruiz, Martín-Polvillo, and Dobarganes 1996). However, the minor volatile compounds formed, in particular carbonyl compounds, are of enormous sensory significance, and may contribute to negatively modify oil flavor (Forss 1972; Frankel 2005).
- At high temperatures, formation of new compounds is very rapid. ROOH are practically absent above 150°C, indicating that the rate of ROOH decomposition becomes higher than that of their formation, and polymeric compounds are formed from the very early stages of heating (Dobarganes 1998). In addition, formation of significant amounts of non-polar TG dimers (R–R), typical compounds formed in the absence of oxygen through interaction of R•, is a clear indication of the low oxygen concentration (Dobarganes and Pérez-Camino 1987).

In summary, as observed in Figure 3.1, two TG radicals, R• formed in the initiation reaction and RO• formed by ROOH decomposition, are involved in the set of termination reactions. This leads to various products of different polarity, stability and molecular weight. Three main groups of compounds can be distinguished by molecular weight, as detailed below.

- TG dimers and oligomers are the most specific compounds in used frying fats, and are formed through interaction between TG radicals. Their molecular weights are higher than those of RH.
- Oxidized TG monomers are TG with at least one of their fatty acyl groups oxidized. They are formed through interaction between TG radicals and hydrogen or hydroxyl radicals. Their molecular weight is similar to the parent non-altered TG (RH).
- Volatile compounds are formed through breakdown of RO• and have molecular weights lower than those of RH.

As previously stated, these reactions take place in the unsaturated fatty acyl groups attached to the glyceridic backbone and, therefore, the stable final products are TG monomers, dimers and oligomers containing modified and non-modified acyl groups. A schematic representation of structures of products formed through oxidative reactions is illustrated in Figure 3.2.

### 3.2.1.1 Triglyceride Dimers and Oligomers

The development of polymerization reactions accounts for the major and most complex group of degradation products found in used frying fats and oils. The complexity results from the different possibilities of oxidation of the unsaturated fatty acids, along with the composition of the fat with a high proportion of TG containing more than one unsaturated acyl group per molecule. It also explains the lack of studies on the structure and formation of TG dimers and oligomers.

Significant information on the mechanisms of polymerization reactions has been limited to the formation of the dimers obtained in the first step of polymerization. The studies were carried out starting from fatty acid methyl esters (FAME) heated

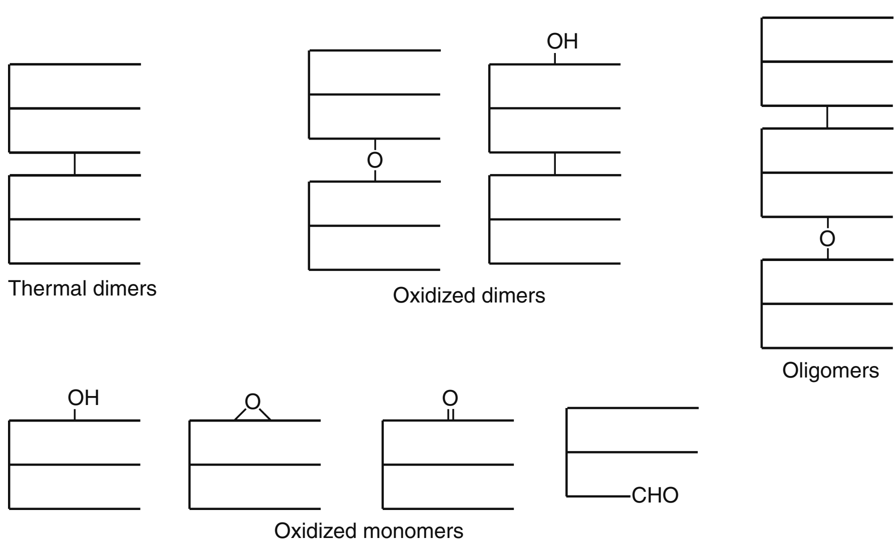



**FIGURE 3.2** Representation of molecular structures of the main groups of compounds formed in frying (schematic).

under well-defined conditions in the absence or presence of air. When heating in the absence of air, the compounds obtained have no extra oxygen, and will be considered separately in the next section on thermal reactions.

The structures of the compounds containing extra oxygenated functions are still largely unknown. Difficulties are due to the heterogeneity in this group of compounds. First, different oxygenated functions are likely to be present in the dimeric linkage or in any other unsaturated fatty acyl group of the molecule. Second, more than one functional group can be present in the same dimeric molecule. Therefore, the large number of possible combinations results in a very complex mixture that is difficult to separate. Under these conditions, studies have paid more attention to the composition of alteration products than to the mechanisms involved in dimer formation. Some of the less complex structures in this group are shown in Figure 3.2.

The basic knowledge on polar dimers has been obtained by heating FAME, TG or fats and oils in air, or by thermal decomposition of FAME hydroperoxides. Among the studies carried out, those giving information on the dimers found in used frying fats and oils or heated under simulated frying conditions are especially interesting (Christopoulou and Perkins 1989a, 1989b, 1989c, 1989d). After separating fractions of different polarity by adsorption chromatography, identification techniques, including mass spectrometry, nuclear magnetic resonance and infrared spectroscopy, have been helpful in providing evidence of some of the dimeric structures formed. The more noteworthy results are outlined below.

- Interestingly, the occurrence of dehydrodimers, bicyclic, tricyclic and Diels Alder non-polar dimers has been reported by different authors (Christopoulou and Perkins 1989a; Ottaviani et al. 1979), suggesting the significance of the allyl radical and formation of non-polar conjugated dienes, even in the presence of oxygen.
- Among products bearing oxygenated functions, acyclic dimers with C–O–C linkages and cyclic dimers such as tetrasubstituted tetrahydrofurans have been isolated from low-polarity fractions obtained after transesterification of heated soybean oil (Ottaviani et al. 1979).
- Structures found for polar dimers were mainly C–C linked dimers containing monohydroxy, dihydroxy and keto groups (Christopoulou and Perkins 1989a).

Structures for compounds with molecular weight higher than that of dimers have not been reported in methyl esters from frying fats or in model systems. This is not unusual considering that much more research remains to be done on structure elucidation and quantification of simpler molecules, i.e., oxidized monomers and dimers, which are intermediates in the formation of trimers and higher oligomers.

#### 3.2.1.2 Oxidized Triglyceride Monomers

Oxidized TG monomers are characterized by at least one extra oxygen atom in at least one of the three fatty acyl chains. They are stable final products resulting from the decomposition of primary oxidation compounds (ROOH). The main functional groups present in frying oils correspond to epoxy, keto, and hydroxy.

The formation of the epoxide ring has been reported to proceed through the reaction of a double bond with an external ROOH (Giuffrida et al. 2004). This mechanism explains the presence of the ring at the site of a double bond, and the concomitant formation of the hydroxy function from the corresponding ROOH. Results from our laboratory support this pathway. Thus, two saturated epoxides, *trans*-9,10- and *cis*-9,10-epoxystearate, were found in samples of methyl oleate and triolein thermoxidized at 180°C. In addition, four monounsaturated epoxides, *trans*-12,13-, *trans*-9,10-, *cis*-12,13- and *cis*-9,10-epoxyoleate, were identified in thermoxidized samples of methyl linoleate and trilinolein (Berdeaux, Márquez-Ruiz, and Dobarganes 1999a). Further results of our investigations showed that the six epoxides, coming from the oleyl and linoleyl chains, make up a major group of oxidation compounds in used frying oils (Velasco et al. 2004b).

As for the hydroxy and keto fatty acyl groups, information is limited due to the complexity provided by structures with a higher number of double bonds, which makes their separation difficult.

Figure 3.2 illustrates schematic representations of the main structures of the oxidized TG monomers. As degradation progresses, more than one oxygenated function may even be present in the same fatty acyl chain, and more than one oxidized fatty acyl group may be present in one TG molecule.

One important subgroup among the oxidized fatty acyl groups are those originated by ROOH breakdown (Kamal-Eldin et al. 1997). Figure 3.3 provides the main mechanism for aldehyde formation from lipid hydroperoxides through homolytic scission of the C–C bonds on either side of the RO•. This cleavage results in two types of aldehydes: volatiles derived from the methyl side of the fatty acid chain, and aldehydes still bound to the TG. The volatile aldehydes have special interest for their contribution to the sensory properties of used frying fats and oils. The formation of non-volatile aldehydes is of enormous chemical and nutritional interest in deep frying because they remain in the oil, are absorbed by the food, and are subsequently ingested. However, their quantitative importance is low compared with other groups of oxidized monomers.

## 3.2.2 Thermal Reactions

Thermal reactions are those taking place without the participation of oxygen. They give rise to products of low polarity, i.e., TG without extra oxygen in the molecule. Even though the frying process takes place in air, many non-polar degradation products have been identified in used frying fats due to the low availability of oxygen at

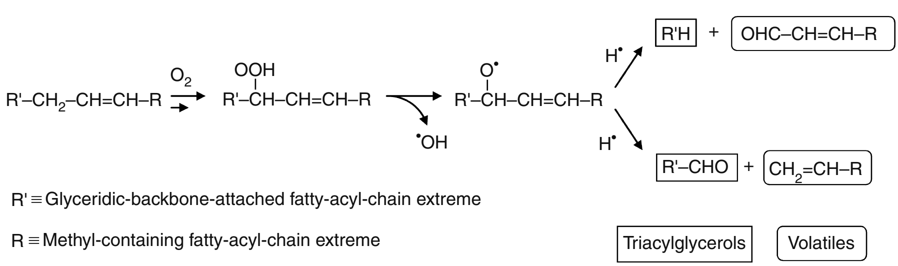



**FIGURE 3.3** Formation of volatiles and short-chain-containing triacylglycerols by scission of hydroperoxides.

high temperature. The main groups of compounds found are TG dimers or isomeric TG, including cyclic or *trans* fatty acyl groups.

#### 3.2.2.1 Non-Polar Triglyceride Dimers

The mechanisms of reaction involved in the formation of non-polar dimers, i.e., products bearing C-C linkages and without extra oxygen in the molecule (Figure 3.2), have been studied by using FAME subjected to high temperatures, usually between 200 and 300°C, in the absence of air to inhibit oxidative reactions. Analysis by mass spectrometry of dimers isolated before and after hydrogenation of samples gave clear information on the rings and the number of double bonds present in the original structures, as well as on isomeric forms. From a large series of experiments, the general conclusions detailed below stand out:

- The major compounds identified during thermal treatment of FAME are generated through radical reactions from the allyl radicals and, consequently, the oxidation pathway is involved in their formation (Figge 1971).
- In the presence of conjugated double bonds, thermal dimers originate after a Diels Alder reaction. Thus, a tetrasubstituted-cyclohexene structure is formed from the reaction of a double bond of a molecule, acting as dienophile, with a conjugated diene of another one (Sen Gupta and Scharmann 1968).
- The proportion of different dimers depends on the conditions. For example, at 140°C, only dehydrodimers were found in significant amounts. Conversely, above 250°C, mono-, bi-, and tricyclic dimers were mainly detected, whereas dehydrodimers were not (Sen Gupta 1969).

Even though thermal conditions in the absence of air are far different from those used in frying, the techniques applied in these studies have been of great help in the identification and quantification of non-polar dimers in used frying fats. The levels found indicate that non-polar dimers may be one of the most relevant groups of new compounds formed during frying (Márquez-Ruiz, Pérez-Camino, and Dobarganes 1990; Márquez-Ruiz, Tasioula-Margari, and Dobarganes 1995). However, the presence of non-polar oligomers in used frying fats has not been reported.

#### 3.2.2.2 Isomeric Triglycerides

The formation of *trans* and cyclic fatty acyl groups above 200°C in the absence of air has been studied in detail and the structures of many compounds identified after derivatization to FAME (Destaillats and Angers 2005a, 2005b; Wolf 1993a, 1993b). Both groups of compounds are present in minor amounts in refined vegetable oils due to the high temperature applied in the deodorization step of the refining process. They basically come from the linoleyl and linolenyl chains (Lambelet et al. 2003; Wolf 1992).

##### *3.2.2.2.1 Trans Isomers*

Formation of *trans* isomers is associated with the complex reactions occurring during partial hydrogenation of polyunsaturated oils (Schmidt 2000). As a result of these reactions, the content of oleic acid and stearic acid increases, and simultaneously

positional and geometric isomers of unsaturated fatty acids are formed. In addition, the formation of *trans* isomers during the deodorization step of the oil refining process has been studied in detail. Non-hydrogenated refined vegetable oils contain variable amounts of *trans* isomers depending on their degree of unsaturation and on the temperature/time conditions applied in their previous processing (Schwarz 2000).

The formation of *trans* isomers during the frying process has been less studied, probably due to the relatively high levels initially present in many fats used for frying. Hydrogenated oils are used for the preparation of many fried products due to their high stability. Today, given the increasing number of foods prefried in hydrogenated oils, *trans* isomeric TGs are usually present in the fat material of these products. Contamination of non-hydrogenated frying media by oil migration from foods previously prefried in hydrogenated oils can result in a source of *trans* compounds (Romero, Cuesta, and Sánchez-Muniz 2000).

When non-hydrogenated vegetable oils are used for frying foods free from *trans* contamination, the levels of *trans* oleic and linoleic isomers are very low, of the order of mg/kg (Beatriz, Oliveira, and Ferreira 1994; Gamel, Kiritsakis, and Petrakis 1999; Sebedio et al. 1996). Hence, when present in significant amounts in fried foods, *trans* fatty acids come from the initial frying fats and are not formed as a consequence of frying conditions.

##### *3.2.2.2.2 Cyclic Isomers*

Numerous cyclic fatty acids are formed in vegetable oils heated at high temperature. They are absorbed extremely well in the intestines of rats and are thought to be toxic, although the levels required to produce a physiologic effect are much higher than those found in used frying fats. This belief stimulated research that has led to a detailed structural analysis of the main cyclic components, and to define the mechanisms of formation. Basic structures originated during frying are cyclohexenyl and cyclopentenyl rings from linolenic acid and a wide variety of cyclopentenyl, cyclopentyl and cyclohexyl compounds, as well as bicyclic fatty acids, from linoleic acid. In addition, small amounts of saturated rings have been detected, suggesting that cyclic compounds can be also generated from oleic acid (Christie and Dobson 2000).

Data from different studies show that contents of cyclic fatty acids in used frying fats and oils may be as low as 0.01–0.66 wt% in oil (Sebedio and Juaneda 2006).

Even though the detection of non-polar isomeric *trans* and cyclic fatty acyl groups is very low, the *trans* isomerization and cyclization are two important reactions affecting the rest of the new compounds formed, i.e., oxygenated compounds formed through thermal oxidation and non-polar dimers formed through thermal reactions.

### 3.2.3 Hydrolysis

Hydrolysis is the well-known reaction affecting fats and oils due to the action of lipolitic enzymes or moisture. In frying, the reaction is of great interest due to the:

- high content of moisture of most foods subjected to frying.
- technological problems originated by the formation of free fatty acids (i.e., decrease of smoke point, formation of extra volatile and flavor compounds, decrease of interfacial tension).

From a nutritional point of view, the compounds formed are not relevant because they are similar to those originated by the action of pancreatic lipase before intestinal absorption.

Hydrolysis is the only reaction breaking down the TG molecule, with formation of diglycerides and fatty acids. Although hydrolysis is one of the simplest reactions during frying, inconsistent results on the variables promoting the formation of free fatty acids have been obtained. For some authors, hydrolysis is the most important reaction during frying (Barbanti, Pizzirani, and Dall Rosa 1994; Pokorny 1998). Nevertheless, in well-controlled frying operations of potatoes under many different conditions, hydrolytic products were minor compounds within the pool of degradation compounds, even though the substrate had a very high content of water (Arroyo et al. 1995; Dobarganes, Márquez-Ruiz, and Pérez-Camino 1993; Pérez-Camino et al. 1991; Sebedio et al. 1990). However, used frying oils with high contents of diglycerides and fatty acids from the fast-food sector have also been reported (Masson et al. 1997). These results indicate that other unknown variables have a much more important effect than the moisture content of the food.

Frying also affects minor components of the oil. For example, phytosterols degrade into a complex mixture of phytosterol oxides that are difficult to separate and quantify. Thus, phytosterol degradation products are another example of the analytical difficulties involved in the separation and quantification of new compounds formed in frying (Dutta et al. 2006). Also, tocopherols, the major natural antioxidants in refined oils, have been studied due to their rapid loss at frying temperatures (Barrera-Arellano et al. 2002). The most important degradation products of tocopherols have been identified in recent investigations (Verleyen et al. 2001; Verleyen et al. 2002).

## 3.3 ANALYSIS OF NEW COMPOUNDS FORMED DURING FRYING AND OCCURRENCE IN USED FRYING FATS

As noted in the introduction, the degradation products differ in polarity from the major compounds initially present in fresh oil, i.e., the non-altered TG. This property is the basis of the determination of polar compounds, the most applied method in the analysis of used frying fats and oils, which gives information on the total amount of the new compounds formed. It consists of the separation by silica column chromatography of a non-polar fraction comprising the non-altered TG and a polar fraction comprising the degradation products. The amount of the polar fraction is determined by the difference in weight from the non-polar fraction.

The group of isomeric TG containing *trans* or cyclic fatty acyl chains is an exception in the evaluation of degradation products by the determination of the polar compounds because their polarity is similar to that of the non-altered TG. Nevertheless, their quantitative significance is minimal compared with the total new compounds formed and, consequently, they do not contribute to significantly modify the measure.

It is, however, necessary to obtain more precise information on the nature and quantity of the new compounds formed during frying because they may impair the nutritional value of the food (Márquez-Ruiz and Dobarganes 2006). For a more detailed analysis, it is necessary to take advantage of the differences in molecular weight among the most important groups of new compounds. In this respect,

high-performance size-exclusion chromatography (HPSEC) is of great utility for direct analysis of the oil (Perrin, Redero, and Prevot 1984) or for analysis of the polar fraction (Dobarganes, Pérez-Camino, and Márquez-Ruiz 1988; Márquez-Ruiz, Pérez-Camino, and Dobarganes 1990).

Table 3.1 summarizes the main techniques applied for the quantification of degradation compounds in used frying fats and oils. When starting from the used frying oil or fat, the polar compounds (IUPAC 1992a) and polymerized TGs (IUPAC 1992b) can be determined. They are the most applied and accepted determinations for the evaluation of the quality of frying oils. A good linear correlation between these two determinations has been found in different investigations (Gertz 2000; Marmesat et al. 2007).

Starting from the fraction of polar compounds (i.e., once the non-altered or non-polar TG have been removed from the sample), analysis by HPSEC allows the concomitant determination of TG polymers, oxidized TG monomers and diglycerides, three groups of compounds clearly differing in molecular weight and associated with the action of temperature, oxygen and the moisture of the food, respectively (Dobarganes, Pérez-Camino, and Márquez-Ruiz 1988; Dobarganes, Velasco, and Dieffenbacher 2000). An alternative technique to reduce the quantity of sample, volume of the solvents, as well as to shorten the time of analysis, is based on solid phase extraction for the separation of the non-polar and polar fractions by using silica cartridges followed by the quantitative analysis of the polar fraction by HPSEC using monostearin as internal standard (Márquez-Ruiz et al. 1996). Only 15 mL of the elution solvents are required for each fraction. This modified procedure is useful for samples with a wide range of alteration products and especially for those of low levels of degradation.

In recent years, a plethora of studies on frying fats and oils based on the application of these methodologies have been published. Results obtained in many samples have shown that, at the level of used frying oil rejection for human consumption (25% polar compounds), TG polymers (i.e., the sum of TG dimers and TG oligomers) are by far the major compounds contributing to the new compounds formed in the frying process, accounting for 12–15 wt% on oil. As for oxidized TG monomers, levels of 7–10 wt% on oil are normally found. Regarding diglycerides, variable contents are reported, but they are of little significance from a quantitative viewpoint (Gertz 2000; Marmesat et al. 2007; Márquez-Ruiz, Tasioula-Margari, and Dobarganes 1995).

The same analytical criteria can be applied to the FAME obtained by derivatization of the oil. When starting from the total FAME, the determination of polar FAME by adsorption chromatography (Dobarganes, Pérez-Camino, and Gutiérrez González-Quijano 1984; Perrin et al. 1985) and analysis of polymerized FAME by HPSEC (Christopoulou and Perkins 1989a) give information on the total fraction of modified fatty acyl chains and on the specific group of polymerized chains, respectively. HPSEC can also be applied to the polar FAME after the separation of the non-polar FAME, i.e., the non-altered chains along with isomeric forms of fatty acyl chains generated through thermal reactions. In this case, the analytical procedure allows concomitant analysis of different groups of polymerized and oxidized fatty acyl chains that form part of the TG molecules (Márquez-Ruiz, Pérez-Camino, and Dobarganes 1990).

**TABLE 3.1**
**Techniques for the Quantitative Determination of Compounds Formed During Frying**

| Sample | Technique | Application | References |
|---|---|---|---|
| Intact used frying fats or oils | Adsorption chromatography | Determination of the total fraction of polar compounds | IUPAC 1992a Standard Method 2.507 |
| | High-performance size-exclusion chromatography | Determination of TG dimers and oligomers | IUPAC 1992b Standard Method 2.508 |
| Polar compounds | High-performance size-exclusion chromatography | Determination of TG dimers, TG oligomers, oxidized TG monomers and diglycerides | Dobarganes, Pérez-Camino, and Márquez-Ruiz 1988; Dobarganes, Velasco, and Dieffenbacher 2000, Márquez-Ruiz et al. 1996 |
| FAME derivatives | Adsorption chromatography | Determination of the total fraction of polar FAME | Dobarganes, Pérez-Camino, and Gutiérrez González-Quijano 1984; Perrin et al. 1985 |
| | High-performance size-exclusion chromatography | Determination of FAME dimers and oligomers | Christopoulou and Perkins 1989a |
| | Gas chromatography | Determination of FAME and short-chain TG bound compounds | Berdeaux, Márquez-Ruiz, and Dobarganes 1999b |
| Polar FAME | High-performance size-exclusion chromatography | Determination of oxidized FAME monomers, FAME dimers and oligomers | Márquez-Ruiz, Pérez-Camino, and Dobarganes, 1990 |
| | Gas chromatography | Determination of epoxy, keto and hydroxy FAME | Velasco et al. 2002; Velasco et al. 2004a |

Analysis of FAME from used frying oils has shown that when oil degradation reaches 25% of polar compounds, the total fraction of polar FAME accounts for 8–10 wt% on oil, being the polymeric FAME the major compounds (5–7 wt% on oil) followed by the oxidized FAME monomers (3–4 wt% on oil) (Márquez-Ruiz, Tasioula-Margari, and Dobarganes 1995).

The next step in the analysis of new compounds formed during frying is the detailed evaluation of the main constituents within the groups of monomers, dimers and oligomers. In this respect, there is a growing interest in the oxidized monomers because of their possible nutritional implications given their high absorbability and their presence in used frying fats at non-negligible levels. In recent years, there has

been increasing evidence that oxidized TG monomers may be detrimental to health, particularly in connection with the development of atherosclerosis, liver damage, and promotion of intestinal tumors (Márquez-Ruiz and Dobarganes 2006).

Short-chain glycerol-bound aldehydes, known as "core aldehydes", have been the most studied oxidized TG monomers because of their potential toxicity. As commented above, their formation proceeds by homolytic β-scission of RO• derived from allylic hydroperoxides (Figure 3.3). Most of the analytical studies have been focused on the intact molecules of TG and other lipid species, and have been very useful to identify the main structures of these compounds and even their occurrence in biological samples (Ravandi et al. 1995; Sjovall, Kuksis, and H. Kallio 2002; 2003). Nevertheless, given the inherent complexity of TG structures, the direct analysis of core aldehydes, as well as of any other group of oxidized TG monomers, does not provide quantitative information. Thus, the same oxidized acyl chain can be present in many very different TG molecules, i.e., molecules with the other two acyl chains different, resulting in a myriad of compounds that are difficult to separate.

Separation and quantification of oxidized compounds should involve previous derivatization of the oil to FAME to eliminate the complexity of the intact TG molecules. From a nutritional viewpoint, this approach is of enormous interest because the oxidation products are absorbed as free fatty acids after the hydrolysis of TG by pancreatic lipase.

Berdeaux, Márquez-Ruiz, and Dobarganes (1999a) studied the quantitative analysis of oxidative products by gas chromatography through derivatization of the oil to FAME. This approach enables grouping fatty acids that originally form part of different TG molecules. Essential requirements of the derivatization step should be good repeatability and recovery of the compounds of interest, as well as not to generate analytical artifacts. Base-catalyzed transesterification at room temperature was selected as the most appropriate derivatization method.

Analysis of n-oxo short-chain FAME, derived from core aldehydes, has received considerable attention because of their potential toxicity, as outlined above. Studies on physiologic effects have been focused on 9-oxononanoic acid (Kanazawa and Ashida 1991; Minamoto et al. 1988). Analytical studies on lipid model systems (Berdeaux, Márquez-Ruiz, and Dobarganes 1999b; Berdeaux et al. 2002) and on thermoxidized and used frying oils (Velasco et al. 2005) have shown that 9-oxo-nonanoate is the major short-chain fatty-acid aldehyde formed at elevated temperature, followed by 8-oxo-octanoate. Samples of used frying oils containing about 25% polar compounds exhibited quantities of 0.61–1.18 mg/g oil for 9-oxononanoate and 0.12–0.23 mg/g oil for 8-oxo-octanoate. The major occurrence of 9-oxo-nonanoate is because the two major unsaturated fatty acids in frying oils, i.e., oleic and linoleic acids, can be involved in its formation through their 9-hydroperoxides. Likewise, any other fatty acid with the first double bound at carbons 9 and 10, such as linolenic acid, may also contribute as precursor of 9-oxo-nonanoate. The formation of 8-oxo-octanoate appears to come only from the 8-hydroperoxide of the oleyl chain, but another pathway was described to justify minor occurrence in model lipid systems consisting of methyl linoleate or trilinolein (Berdeaux, Márquez-Ruiz, and Dobarganes 1999b).

Besides the short-chain FAME aldehydes, short-chain fatty-acyl groups containing a terminal carboxylic group (free or esterified) were identified and quantified

(Berdeaux, Márquez-Ruiz, and Dobarganes 1999b; Berdeaux et al. 2002; Velasco et al. 2005). After the base-catalyzed transmethylation step, methylation with diazomethane gave rise to considerable contents of two saturated dimethyl diesters of 8 and 9 carbon atoms, respectively, i.e., dimethyl suberate and dimethyl azelate. Quantitative analysis of these compounds obtained by transmethylation followed by methylation with diazomethane accounts for the free and esterified forms of the carboxylic group because the esterified form, which characterizes a group of compounds known as estolides, comes into the corresponding dimethyl diester in the transmethylation step. It was suggested that these species can come from further oxidation of corresponding 8-oxo-octanoate and 9-oxo-nonanoate, respectively. Contents in used frying oils containing about 25% polar compounds were 0.08–0.28 mg/g oil for dimethyl suberate and 0.33–0.96 mg/g oil for dimethyl azelate (Velasco et al. 2005).

As commented above, analysis of FAME has allowed quantification of six compounds bearing the epoxy function that come from the oleyl and linoleyl chains of TG (Berdeaux, Márquez-Ruiz, and Dobarganes 1999a; Velasco et al. 2002; Velasco et al. 2004a, 2004b). Evaluation of used frying oils with levels of polar compounds of about 25% showed values between 3.37 mg/g and 14.42 mg/g oil for the total content of the six epoxy FAME compounds, which indicates that these compounds are a major group within the fraction of oxidized monomers (Velasco et al. 2004b).

Another two groups of compounds analyzed in a similar way have been FAME with 18 carbon atoms bearing the hydroxy or keto function. Along with the epoxy FAME, the total content of these three groups of compounds has been found to be 1.5–3.5 wt% on oil in samples containing 25% polar compounds (unpublished results).

## 3.4 INTERACTIONS BETWEEN THE FOOD AND THE FRYING OIL

Despite the present guidelines which recommend decreasing the level of fat in the diet and the undesirable modifications of the frying medium, fried foods have become increasingly popular, mainly due to their organoleptic characteristics, which are appreciated by consumers. In this section, the multiplicity of changes contributing to the characteristics of the fried food due to the interaction between the frying medium and the food components are considered.

### 3.4.1 Major Changes in the Food: Water Loss and Oil Uptake

Frying is considered to be essentially a dehydration process where the oil provides an effective medium of heat transfer. Under these conditions, a part of the frying oil is absorbed by the food, contributing considerably to the quality of the fried product. The temperature of the frying oil decreases as a result of food addition, and the temperature inside the food increases slowly, remaining at about 100°C as the water is flowing from the core to the external layers. Steam limits the penetration of oil inside the food, resulting in a fried product where two characteristic zones can be defined: the dehydrated surface (where the main changes occur) and the core (where temperature does not pass 100°C).

The main parameters influencing water loss and oil uptake are temperature and time. It has been found that temperature has no significant effect between 150°C and 180°C (Varela 1977). However, it is generally accepted that the higher the temperature, the lower the oil absorption on the surface and, on the contrary, excess of oil absorption may result from low frying temperatures. Interrelation of temperature and time is common in frying so, the higher the temperature, the shorter the time to obtain a similar fried product.

Apart from the parameters established for food preparation, water loss and fat absorption depend on the food and the frying oil. With respect to the food, many variables affect the final composition of the finished product. These variables include food composition, surface structure and surface composition, moisture and lipid contents, product shape, surface-to-weight ratio, porosity and prefrying treatment (Fillon and Henry 1998; Saguy and Dana 2003). For example, even for a single non-lipid food such as potatoes, oil absorption and water loss strongly depended on their specific gravity—oil uptake being lower as the specific gravity increases—as well as on the surface-to-weight ratio exposed to the frying medium: the larger the ratio, the higher the oil absorption (Guillaumin 1986). Thus, there are many variables that are difficult to control that affect the oil content of fried foods, and therefore their overall effect is not easy to foresee. Oil absorption can vary from as little as 6% (e.g., in roasted nuts) to about 40% (e.g., in potato crisps) (Saguy and Dana 2003).

The influence of the type of fat or oil used is lower than that of the food. In general, oil absorption depends more on oil quality than on oil type. Influence of oil quality is attributed to formation of degradation compounds, which increase the polarity of the frying medium. This is the basis of the surfactant theory, which tries to explain the basis of the oil uptake and its relationship with the quality of fried food.

According to Blumenthal's theory, surfactants are the main agents responsible for the quality of the final fried product. There is a relationship between the quality of the fried food and the amount of surfactants, i.e., amphyphilic compounds like soaps, phospholipids, diglycerides, formed as the oil degradation increases or leached from the food. Thus, when the oil is fresh and there are no surfactants or their level is very low, heat transfer is difficult because there are no compounds facilitating the contact between the two immiscible media, i.e., the oil and the water leaving the food. Under these conditions, there is little oil absorption and the color of the food remains pale. Once the oil degradation starts and the level of polar compounds increases, the contact between the oil and the food is improved until optimal conditions, consisting of a thin and crispy crust, a golden color and a delicious flavor. If the degradation increases and the level of surfactants is too high, the product can become unacceptable because of a high content of oil absorbed and a darkened and thick crust (Blumenthal 1991; Blumenthal and Stier 1991; Stier 2000; 2004).

Other alternative mechanisms have been proposed in various studies to describe oil absorption phenomena. For example, it has been proposed that as water is removed from the food, the oil adheres and enters the large voids formed. Another mechanism is based on a cooling-phase effect taking place once frying has finished and the food is removed from the fryer. Water vapor condenses when the product

starts to cool down, decreasing the internal pressure. Oil adhered to the food surface is sucked in due to a "vacuum effect." Therefore, oil uptake is a surface phenomenon involving equilibrium between adhesion and drainage of oil as the food is removed from the oil bath. This subject has been recently reviewed by Dana and Saguy (2006).

Due to consumer preferences for low-fat foods and fried foods, a great effort has been made on two different aspects. Firstly, theoretical studies have been carried out to explain transport phenomena in different surfaces by mathematical models (Bouchon and Pyle 2005a, 2005b; Farinu and Baik 2005; Hindra and Baik 2006; Vitrac et al. 2002; Yamsaengsung and Moreira 2002a, 2002b; Yildiz, Palazoglu, and Erdogdu 2007). Secondly, studies have been conducted to decrease oil uptake through modification of the external surface, either by specific treatments (Debnath, Bhat, and Rastogi 2003; Moyano and Pedreschi 2006; Rimac-Brncic et al. 2004) or by changing the coating composition (Akdeniz, Sahin, and Sumnu 2005; Albert and Mittal 2002; Mellema 2003; Sanz, Salvador, and Fiszman 2004).

### 3.4.2 Migration of Food Components to the Frying Oil

As commented above, the quality of fried food is greatly affected by the quality of the frying oil, although the influence of the food on the quality of the oil may be of similar importance.

#### 3.4.2.1 Migration of Minor Compounds

Minor components of the food leaching into the frying oil may easily modify the performance and quality of the oil. Although it is not easy to find studies addressing the specific effect of minor compounds from foods, interesting information can be found in general reviews (Fillon and Henry 1998; Pokorny 1980; 1998; 1999). Among the main compounds contributing to modify physical or chemical properties of the frying oil, the groups mentioned below stand out:

- Amphyphilic compounds such as phospholipids and other emulsifiers can contribute to early foaming.
- Lipid-soluble vitamins and trace metals leaching into the frying oil inhibit or accelerate oil oxidation depending on their antioxidant or prooxidant effect.
- Cholesterol from fatty animal foods is found in frying vegetable oils and can be incorporated in non-fatty foods during subsequent frying.
- Pigments and Maillard browning products can modify the susceptibility against oxidation of the frying oil and contribute to darkening.
- Phenolic compounds present in the foods or in added spices can increase the stability of frying oil.
- Volatile compounds from strongly flavored foods such as fish or onions can contribute to special off-flavors.

Finally, apart from migration of lipids from the food into the frying oil, foods which are breaded or battered may contribute with particles, resulting in burning, off-flavors and increasing oil degradation.

#### 3.4.2.2 Fat Interchange During Deep Frying of Fatty Foods

From a quantitative viewpoint, frying oil can be mainly affected by contamination with fats or lipids from foods. Two different types of fatty foods will be considered. First, natural fatty foods such as fish and meat, which are normally coated by batter or bread and characterized by a low content of lipids on their surface, will be discussed. Then, the increasing group of frozen prefried foods (potatoes, fish, vegetables), where the fat or oil is mainly located on the surface, will be outlined. Lipid exchanges, as well as final lipid composition and quality, may be very different in both groups of foods.

##### *3.4.2.2.1 Natural Fatty Foods*

Great differences can be found in the lipid composition of the food depending on the method of frying, type of food and surface composition, i.e., batter, bread or uncoated food. For example, it has been found that battered fish absorbs less oil than breaded fish. The reason seems to be the rapid formation of a crust in the battered food that impedes the transfer of oil and water, while the thickness of coating in breaded fish is much lower and less protective (Makinson et al. 1987). As a consequence of variable fat absorption, it is difficult to forsee the fatty acid composition of the final product. In this respect, the higher the content of oil absorbed, the closer the lipid composition of the fried food to that of the frying oil.

Even more important from the nutritional viewpoint is the possible diffusion of food lipids into the frying oil during the process. Lipid interchange is obvious in foods like meat or chicken whose lipid content may even be lower after frying (Henry 1998). Minor compounds of these foods in the frying oil, such as cholesterol, phospholipids and vitamins, accounts for lipid exchange. Surprisingly, there is no information on this aspect in detailed studies on lipid changes during fish frying (Dobarganes, Marquez-Ruiz, and Velasco 2000), even though lipid exchanges can be easily approached from the fatty acid compositions of the food before and after frying (Pérez-Camino et al. 1991). Taking lipid exchange into consideration in published results, it can be seen that a significant proportion of the initial food lipids passes into the frying medium, mainly from fatty fish with high lipid content. Consequently, from a nutritional viewpoint, great care should be taken regarding the composition of the dietary fat ingested because lipid exchange may contribute to modify the fatty acid composition of the finished product, being in a few cases quite different from that of the initial food.

##### *3.4.2.2.2 Frozen Prefried Foods*

Given the increase in the consumption of frozen prefried foods, lipid exchanges in the final frying operation of these products are of special interest. The lipid constituents have two specific characteristics:

- Prefried products contain significant amounts of absorbed used frying fat or oil of unknown composition and quality, depending on the variables of the prefrying process.
- As a consequence of the previous frying process, the oil is preferably absorbed in the external layers of the food and thereby lipids are in contact with the frying oil during the second frying.

Fat absorption, lipid interchange and possibilities of preferential adsorption of polar compounds on the food surface during frying of frozen prefried foods have been studied in detail (Marmesat et al. 2005; Pérez-Camino et al. 1991; Pozo Díez et al. 1995; Sebedio et al. 1990). As outlined above, fat absorption clearly depended on the type of food, whereas similar levels of polar compounds, polymers and minor compounds were found between the lipids extracted from fried foods and the corresponding frying oils. Furthermore, a similar fatty acid profile was found between the oil and the food fried in it, indicating that lipid interchange was very high. When the fatty acid profile of the frozen prefried food and that of the oil used for frying were very different, the initial lipids remaining in the fried product and those being transferred to the frying oil could be calculated with high accuracy (Pérez-Camino et al. 1991). Irrespective of the oil used and of the prefried food subjected to frying, >90% of the fried food lipids came from the frying oil, whereas >85% of the prefried food lipids were released into the frying oil.

### 3.4.3 Chemical Interactions between the Frying Oil and the Food

Although outside of the scope of this chapter, the main reactions contributing to the appreciated golden browning of fried foods are considered to be those between proteins and carbohydrates in the complex mechanism of the Maillard reaction. Due to analytical difficulties to define the macromolecules contributing to the color of the fried foods, interesting information on the compounds involved is not available. In the last few years, studies related to the Maillard reaction in fried foods have focused on the occurrence and quantitative analysis of acrylamide because of its potential toxicity. The formation of the latter during frying is considered in detail in Chapter 7.

One aspect of particular interest is the influence of the Maillard reaction products migrating to the frying medium on the oxidative stability of the oil. Several studies have shown that Maillard products exert antioxidant activity in model systems and foods (Zamora and Hidalgo 2005), but very little in connection with this subject has been reported on frying oils (Marmesat et al. 2005; Wagner et al. 2002). In a recent study, the oxidative stability index of high oleic high palmitic sunflower oil, as measured by the Rancimat device at 120°C, substantially increased after the discontinuous frying of almonds, peanuts and sunflower seeds. Marmesat et al. (2005) suggested that Maillard products could be involved in the increased stability of the frying oil.

Frying oil can also take part in the non-enzymatic browning by reaction of lipid oxidation products with amines, amino acids and proteins (El-Zeany and Fattah 1982; Gillatt and Rossell 1992; Hidalgo and Zamora 2000; Pokorny 1998; Zamora and Hidalgo 2005).

Lipid radicals and secondary lipid oxidation products including aldehydes, epoxides, and ketones have been described to react with reactive groups of amino acid residues (Gillatt and Rossell 1992; Hidalgo and Zamora 2000; Pokorny 1998). Formation of compounds of low molecular weight and high molecular weight polymers is involved in the non-enzymatic browning resulting from the interaction between oxidized lipids and proteins, although the relative contribution of both types of

products is unknown (Hidalgo and Zamora 2000). The main mechanism of reaction is illustrated in Figure 3.4. The carbonyl compounds derived from unsaturated lipids condense with free amino groups to produce imino *Schiff* bases that polymerize by repeated aldol condensation to form brown pigments.

An additional mechanism based on the interaction of epoxyalkenals with amino groups of proteins has been proposed to explain the formation of polypyrrolic polymers contributing to the non-enzymatic browning, as well as the generation of volatile heterocyclic compounds (Hidalgo and Zamora 1995a, 1995b; Zamora and Hidalgo 1994, 1995). Although it has been shown that epoxides are one of the major functional groups detected in thermoxidized and used frying oils (Velasco et al. 2004a, 2004b), the occurrence of epoxyalkenals at frying conditions has not been reported, and therefore their contribution to the non-enzymatic browning of fried foods is unknown.

Most of the studies on the non-enzymatic browning have been conducted in model systems, so the extent of the reactions involving lipid oxidation products and the Maillard reaction under the real conditions of the frying process is unknown. This is mainly because the reaction products are macromolecules of difficult extraction and the extraordinary number of compounds involved makes analysis difficult. Furthermore, these two reaction pathways are influenced by each other, have common reaction intermediates and give rise to similar products. Recently, in a detailed review on the subject, it has been suggested that both reactions are so interrelated that they should be considered simultaneously (Zamora and Hidalgo 2005).

The state of oxidation of the oil seems to have a key role in the browning developed in frying, but such a role is ascribed to a physical phenomenon occurring due to the interfacial activity of lipid oxidation compounds. The location of oxidation

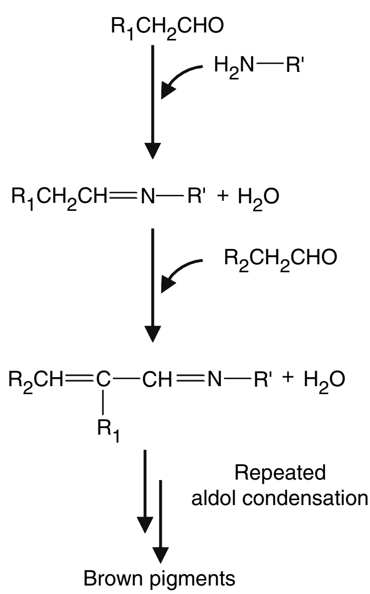



**FIGURE 3.4** Contribution of lipid oxidation products to non-enzymatic browning.

products at the oil–food interface allows a greater contact between the two phases and consequently a better transfer of heat that facilitates browning. As outlined above, this is the basis of Blumenthal's theory (Blumenthal 1991; Blumenthal and Stier 1991).

## 3.5 CONCLUSIONS

Chemical changes occurring in fats and oils during frying involve the formation of a great variety of new compounds. Among them, TG dimers and oligomers are the major and more specific compounds. Determination of the main groups of compounds, i.e., oxidized, polymerized and hydrolytic compounds, by a combination of adsorption and size-exclusion chromatographies constitutes the best tool for the analysis of used frying fats and oils because it allows evaluation of the relative importance of the main pathways of degradation. Efforts during the last decade have been directed to gain information on the rate of formation of new compounds in relation to the conditions of frying, and also to explain transport phenomena during frying to decrease oil absorption by the food. However, much work remains to be done to clarify the specific structures of the new compounds formed during frying, particularly those present in the food due to the interaction between oxidized compounds and food proteins.

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# 4 Quality of Frying Oil

*Stavros Lalas*

## CONTENTS



## 4.1 INTRODUCTION

Deep-fried foods are becoming increasingly popular all over the world. Frying is one of the oldest methods known for preparing food. It is useful for cooking many food types: meat, fish and vegetables (Rossell 2000). Among the most commonly fried foods at home and in restaurants are potato chips and fish (Lalas and Dourtoglou 2003). Commercial deep-fat frying is estimated to be a billion-dollar

industry worldwide. This includes not only oils, fats, and shortenings used for frying, but also the commercial and retail value of foods fried at the industrial, food service or restaurant level (Blumenthal 1996).

Deep-fat frying is the most complex application of edible fat and oil (Gertz 2000). Some desirable (as well as undesirable) chemical compounds are formed in the oils during frying (Pokorny 1989). Frying fat influences the quality of the finished product such as flavor, texture, shelf-life and nutritional attributes (Dunford 2003), as well as storage stability. Products of oil oxidation are strong catalysts and cause further degradation of the oil (contained in the product) during storage, especially if the oil is abused in the frying process (Gupta 2005).

The fats used for frying range from non-hydrogenated fully refined fats and oils to specially hydrogenated products designed for frying. Contribution of no off-flavors and ease of handling are the major criteria for selecting a frying fat for a given application (Dunford 2003). Additionally, the availability and cost of oil are extremely critical for the industry. Even the best-performing frying oil is not beneficial to the business if it is not available in sufficient quantities (Gupta 2005). Specific requirements of a product, such as appearance, seasoning adhesion, mouth feel, and fat retention, are also important considerations for selection of frying oil (Dunford 2003). There are also regional preferences for particular oils used for frying foods. The type of frying fats used once depended almost exclusively on where people lived (Blumenthal 1996), i.e., oil availability and the flavor of oil they were accustomed to. For example, for chips, cottonseed oil is used in the USA; groundnut oil in the Indian subcontinent; olive oil in the Mediterranean region; and fats of animal origin in Northern Europe (Blumenthal 1996; Gupta 2005).

It is important to assess frying oil quality because a certain amount of oil is absorbed by food during frying. The oil used in the frying operation becomes part of the food and is the major factor in the quality and nutritional value of this food (Rossell 2000). The degraded oil has an altered nutritional and toxicological profile when compared with fresh oil (Perkins and Kummerow 1959). Determination of its quality is therefore critical for achieving the desired shelf-life for the product, and reduces the potential for creating health hazards (Gupta 2005).

In this chapter, the factors affecting the quality of frying oil are presented. The changes occurring during frying, different kinds of deterioration, and various products of degradation, are reviewed. A thorough description of the various methods used to determine frying oil quality is then discussed. Finally, a brief section concerning antioxidants that can be used to retain the quality of oil used for frying is given.

## 4.2 CHANGES OCCURRING DURING FRYING

Three main factors play a part in the frying process: the food to be fried; the oil used; and the characteristics of the process, especially temperature and frying time (Blumenthal 1991; Robertson 1967).

During deep frying, the oil is exposed continuously or repeatedly to elevated temperatures in air and moisture. Numerous chemical reactions, including oxidation and hydrolysis, occur during this time, as do changes due to thermal decomposition.

As these reactions proceed, the functional, sensory and nutritional quality of the oil changes and may eventually reach a point where it is no longer possible to prepare high-quality fried products, and the frying oil must be discarded (Stevenson 1984). Chang, Peterson, and Ho (1978) and Landers and Rathman (1981) reported that the chemical reactions taking place during deep oil frying differ from those that occur when the oil is heated continuously. Thus, reactions occurring in studies conducted with oils heated in air, with or without agitation, may not be representative of those of the same oils used under normal intermittent frying conditions.

The decomposition products formed during frying can be divided into two broad classes: volatile and non-volatile products.

### 4.2.1 Volatile Decomposition Products

Volatile decomposition products (VDP) include aldehydes, ketones, alcohols, acids, esters, hydrocarbons, lactones, and aromatic compounds.

Most of the VDPs are removed from the frying medium by the steam generated during frying (Stevenson, Vaisey-Genser, and Eskin 1984). However, Chang, Peterson, and Ho (1978) reported that some of these products are retained in the fried food and also inhaled by the deep-frying operator, and could therefore have an effect on the health of these individuals.

### 4.2.2 Non-Volatile Decomposition Products

Non-volatile decomposition products (NVDP) comprise the second class of products formed during deep frying. Their formation is due largely to thermal oxidation and polymerization of the unsaturated fatty acids in the frying medium. This is of concern because these products not only remain in the frying oil to promote further degradation, but are also absorbed by the fried food and therefore consumed (Gertz 2000; Stevenson, Vaisey-Genser, and Eskin 1984).

Paradis and Nawar (1981) reported that compounds of higher molecular weight are more reliable indicators of oil abuse because their accumulation is steady and they have low volatility. The formation and accumulation of NVDPs are responsible for physical changes in the frying oil (e.g., increase in viscosity, color and foaming) as well as chemical changes (e.g., increase in free fatty acids (FFAs), carbonyl value, hydroxyl content, saponification value; and decrease in unsaturation) with resulting increase in the formation of high molecular weight products.

Various types of reactions are responsible for these changes in the quality of frying oil. The color of the frying medium and the nature of the composition of the oil may be altered by the solubilization of colored compounds and lipid materials in the food being fried.

Perkins (1967) and White (1991) reported that oxidation is accelerated at the high temperatures used in deep frying. When oil is heated in air, it first shows a gain in weight as oxygen is absorbed, and its peroxide value may increase. As heating continues, the peroxides decompose, and scission products start to distil off, leading to a net loss in weight.

Hydroperoxides may undergo further degradation of three major types: (a) fission to form alcohols, aldehydes, acids and hydrocarbons, thereby also contributing to the

darkening of the frying oils (color has been attributed to α-, α- and α-, α′-unsaturated carbonyl compounds) and flavor changes; (b) dehydration to form ketones; and (c) free-radical formation of dimers and trimers, leading to polymers, all of which contribute to viscosity increase. The rate of viscosity increase parallels the rate of polymer formation. Artman (1969) reported that the ultraviolet absorption of the oil increases owing to conjugation of the double bonds and the accumulation of oxygenated products. The iodine value of the oil may rise during the early stages of thermal oxidation because of the formation of new unsaturated linkages, but it later falls as the double bonds are consumed in various reactions.

Unsaturated fatty acids are mostly affected during the frying process (Gupta 2005). The rate of oxidation is roughly proportional to the degree of unsaturation of the fatty acids present. Linolenic acid (three double bonds) is therefore much more susceptible than oleic acid (one double bond). Moisture in the foods being fried also causes some hydrolysis, which results in the formation of FFAs, monoglycerides, diglycerides and glycerol. FFAs may also be formed during oxidation due to cleavage and oxidation of double bonds (Perkins 1967).

Moisture also has a positive effect because it creates a "steam blanket effect" over the fryer, thereby reducing contact with air as well as helping to remove peroxides, flavors and odors that would otherwise accumulate in the frying oil (Stevenson, Vaisey-Genser, and Eskin 1984).

The final type of change in the quality of frying oil takes place due to heat that accelerates the formation of dimers and cyclic compounds through polymerization. Although the mechanisms are very complex and incompletely understood, the compounds that result from this process are large molecules formed by carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges between several fatty acids (Landers and Rathman 1981), increasing the concentration of polar compounds.

Marked increases in these compounds contribute to increases in oil viscosity, foaming, "gum" accumulation and color darkening (Stevenson, Vaisey-Genser, and Eskin 1984).

## 4.3 DETERIORATION OF FRYING OILS

In frying, the food is submerged in oil heated in air, and as such, the oil is exposed to the action of three agents that cause the most drastic changes in structure: (i) moisture from the foodstuff, giving rise to hydrolytic alteration; (ii) atmospheric oxygen entering the oil from the surface of frying pan, giving rise to oxidative alteration; and (iii) the high temperature at which the operation takes place, which results in thermal alteration (Gere 1982; Lillard 1983).

Hydrolysis involves breakage of the ester bond with consequent formation of FFAs, monoglycerides, diglycerides and glycerol, but the oxidative and thermal degradations take place in the unsaturated chain constituents of the triglycerides with at least one of their three acyl radicals altered.

The three types of alteration are not only superimposed, but are also interrelated. High temperature plays a large part in the oxidation products, favoring the formation of oxidative and non-oxidative dimers and polymers and, in the same way, the FFAs originated in the hydrolysis are more susceptible to oxidative and thermal alteration than if they are esterified in the glycerol (Gutierrez, Gonzalez,

and Dobarganes 1988). The degradation products, as reported above, belong to two groups: (i) volatile compounds, which by their nature are partly eliminated during the frying process, and whose importance is intimately related with the organoleptic characteristics of the oil and the fried product; and (ii) non-volatile compounds, which are of interest as much as from the nutritional viewpoint because they accumulate from the beginning of frying, and their level is related to the total oil alteration.

Belitz and Grosch (1987) compiled the reaction types involved in, and responsible for, the changes in oil and fat structures during frying. Specifically, these reactions are autoxidation (autoxidation, photoxidation or enzymic), isomerization, polymerization and hydrolysis (hydrothermal or enzymic) which produce volatile compounds (acids, aldehydes, esters, alcohols), epoxides, branched-chain fatty acids, dimeric fatty acids, mono- and bicyclic compounds, aromatic compounds, compounds with *trans* double bonds, hydrogen, carbon dioxide, FFAs, monoacylglycerols and diacylglycerols, and glycerol.

### 4.3.1 Hydrolytic Rancidity

Hydrolysis leads to hydrolytic rancidity and involves hydrothermal hydrolysis to FFAs and other products.

Hydrolysis is the major chemical reaction that takes place during deep-oil frying. It occurs when food is fried in hot oil. Water, which is present as steam, attacks the triglycerides, which are hydrolyzed to FFAs, monoacylglycerols, diacylglycerols and glycerol (Roth and Rock 1972). Hydrolysis can also take place by the action of lipase enzymes.

Low levels of FFAs are not necessarily objectionable, particularly if they are 16C- or 18C-fatty acids as commonly found in soybean or corn oil. However, for other fats such as coconut oil, low levels of shorter carbon-chain fatty acids may be quite objectionable. Hydrolytic rancidity is not as important in oils containing predominantly fatty acids of longer chain-length except when they are used as frying media (Robards, Kerr, and Patsalides 1988).

During frying, when heat and water are present, FFAs may develop rapidly if poor processing techniques are adopted. Moreover, there is no additive that effectively prevents formation of FFAs. Antioxidants will not prevent formation of FFAs owing to chemical hydrolysis.

### 4.3.2 Oxidative Rancidity

Oxidative rancidity results from more complex lipid oxidation processes. According to Belitz and Grosch (1987), the autoxidation mechanism has several fundamental steps. The oxidation process is essentially a radical-induced chain reaction divided into initiation, propagation, branching and termination steps. During the initiation phase, molecular oxygen combines with unsaturated fatty acids to produce hydroperoxides and free radicals, both of which are very reactive. For this phase to occur at a meaningful rate, some oxidative initiators must also be present, such as chemical oxidizers, transition metals (i.e., iron or copper) or enzymes (i.e., lipoxygenases). Heat and light also increase the rate of this and other phases of lipid oxidation. The reactive products of this initiation phase will, in turn, react with additional

lipid molecules to form other reactive chemical species. The propagation of further oxidation by lipid oxidation products gives rise to the term "auto-oxidation" that is often used to refer to this process. In the final, termination phase of lipid oxidation, relatively unreactive compounds, including hydrocarbons, aldehydes, and ketones, are formed

Autoxidation is mainly responsible for rancidity in frying oils. The classical route of autoxidation depends on the production of free lipid radicals from triglycerides (or fatty acids formed by hydrolytic rancidity) by their interaction with oxygen.

The autoxidation of oils at temperatures $< 80^{\circ}C$ has been the subject of extensive investigations (Buck 1981; Dugan 1976; Gunstone and Norris 1983; Heimann 1980; Labuza 1971; Swern 1961). Of particular importance, however, is the oxidative behavior of unsaturated fatty acids at relatively high temperatures, such as in frying. The reactions which take place and the chemical compounds produced under these conditions have obvious implications with regard to flavors and off-flavors (Nawar and Witchwoot 1980).

Saturated and unsaturated fatty acids may undergo chemical decomposition when exposed to heat in oxygen.

The length of the induction period and the rate of oxidation are affected by the following factors: increases in temperature; irradiation; increasing surface–volume ratio; catalysts or initiators such as preformed hydroperoxides, chlorophyll or transition metals; and the fatty acid composition of the oil. The more allyl groups that are present, the shorter is the induction period, and the higher the oxidation rate.

## 4.3.3 Thermal Oxidation

Various products can be formed as a result of thermal oxidation. Oxidation of oil at high temperature differs from oxidation of the same oil at low temperature. Not only are the reactions accelerated at high temperatures, but also quite different reactions take place. This is because the initial oxidation products which form at low temperatures are too unstable to exist more than transiently at high temperatures.

### 4.3.3.1 Volatile Products

Autoxidation of an unsaturated fatty acid results in the formation of various monohydroperoxide isomers. According to Grosch (1987), the volatile compounds are formed by the decomposition of the monohydroperoxides by homolytic reactions.

According to May, Peterson, and Chang (1983) and Selke, Rohwedder, and Dutton (1977), the classes of compounds which belong to volatiles include aldehydes, ketones, alcohols, monobasic acids, esters, hydrocarbons, lactones and aromatic compounds. Volatile products have been of interest chiefly because of their potent and undesirable flavor properties.

### 4.3.3.2 Cyclic Compounds

Cyclic compounds are di-substituted cyclic fatty acids (one substituent being a propyl group) having one ethylenic bond in the 6-carbon-membered ring, and the other one on the substituent having the acid function.

#### 4.3.3.3 Dimers and Polymers

As oils undergo oxidation and heat stress during the frying operation, dimers and polymers can be formed in the oil which lead to changes in molecular weight, viscosity and heat-transfer efficiency of the oil, and affect the quality of products fried in it.

According to Lillard (1983), polymers can originate by the "Diels–Alder" reaction. This reaction involves the olefin group of one fatty acid and a *trans-trans*-conjugated diene fatty acid. Conjugated diene fatty acid can result from heat or an oxidation reaction. Any of the free radicals produced in lipid oxidation also react to form polymers.

Formation of these cyclic dimers, non-cyclic dimers or other polymeric compounds may involve carbon–carbon and carbon–oxygen bonding. These reactions can occur between FFAs, between fatty acids on the same triglyceride, or between fatty acids of different triglycerides. According to Belitz and Grosch (1987), under deep-frying conditions, the olefinic fatty acids are isomerized into conjugated fatty acids which in turn interact by a 1,4 cycloaddition, yielding "Diels–Alder adducts." Polymers may also contain hydroxy, oxo or epoxy groups.

Such compounds are undesirable in deep-frying oil because they persistently diminish the flavoring characteristics of the oil and, because of their HO-groups, behave like surface-active agents, causing foaming.

## 4.4 DETERMINATION OF FRYING OIL DETERIORATION

The process of frying is a complex system that depends on the extent of chemical reactions such as oxidation, polymerization, and hydrolysis, which cause changes in the physical and chemical properties of the heated fats during frying (Gertz 2000). Because the assessment of the quality of frying oil based on visual inspection, wherein the cook employs experience to decide when to change the oil based on color, odor, excessive foaming, smoking and by tasting the food products, proved inadequate and unreliable due to its subjective nature (United States Patent 1998), various methods (chemical tests, instrumental methods, physical methods and rapid tests) have been proposed to determine the chemical, physical and other parameters of frying oil.

According to Paradis and Nawar (1981), simple, objective methods for quality evaluation of used frying oil are important. In the food industry, a significant economic advantage can be gained from determining when frying oil is no longer suitable for use.

There are many methods for analyzing heat abuse of a fat or oil. The methods chosen depend on the accuracy of measurement desired, the money available for establishing and running the tests, and the time allowed. Perhaps more important, the method chosen will depend on the purpose for measuring the frying oil. Quality-control operators may desire much less detail and may need less accuracy than research scientists who are conducting laboratory studies.

Chemical methods mainly measure the build-up of certain products of oxidative and thermal deterioration in frying oils that have taken place as indices of rancidity. Physical methods measure the changes that occur in frying oil over time;

most are due to a build-up of polymers. Other methods such as sensory evaluation, conjugates dienes, and the thiobarbituric acid (TBA) test are also used. Some tests are instrumental.

The parameters described below are indicators of the state of oil deterioration. However, none of these parameters can judge frying life adequately in all situations. The inadequacy of monitoring a single property of the oil to measure the overall quality of frying oil has been highlighted by many researchers (Miyagawa, Hirai, and Takezoe 1991; Wu and Nawar 1986).

### 4.4.1 Peroxide Value

The primary products of lipid oxidation are hydroperoxides, which are generally referred to as "peroxides". Peroxides are unstable organic compounds formed from triglycerides. The peroxide value is the classical method for determining the extent of oil oxidation (Lawson 1985; Rossell 1983) and measures the formation of intermediate hydroperoxides in milliequivalents of active oxygen per kilogram of sample. Hydroperoxides formed by fat oxidation react with iodide ions to form iodine, which in turn is measured by titration with thiosulphate.

The peroxide value serves as an indicator of oil quality. Although it does not distinguish between the various unsaturated fatty acids that undergo oxidation and does not supply information about the secondary oxidative products formed by hydroperoxide decomposition, generally it can be stated that the peroxide value is an indicator of the primary level of oil oxidation.

The change in peroxide values versus time exhibits an induction stage, where a steep increase in peroxide value occurs, and a decrease as lipid oxidation proceeds. Hydroperoxides break down at a faster rate than their formation. Low-quality oil will have shorter induction periods (Sheabar and Neeman 1988).

According to Lea (1952), the two principal sources of error in peroxide value method are the absorption of iodine at unsaturated bonds of the fatty acids, and the liberation of iodine from potassium iodide by oxygen present in the solution to be titrated. The latter is often referred to as the "oxygen error," and leads to higher peroxide values. Another problem with using peroxide values is that they increase after the sample is removed from the fryer (Fritch, Egberg, and Magnuson 1979; Gray 1978).

Peroxides are unstable under frying conditions. An increase in the peroxide value during the initial stage of frying would be expected to be followed by a decrease with further frying because the hydroperoxides tend to decompose at 180°C to form secondary oxidation products (Chatzilazarou et al. 2006; Perkins 1967; Tsaknis et al. 1998a). Further frying results in another increase in peroxide value. The overall increase in peroxide value occurs particularly during the cooling period, where the frying oil is exposed to air at high temperature (Augustin and Berry 1983). Peroxide and hydroperoxides, although flavorless, provide an indication of impending flavor deterioration (Gray 1978).

### 4.4.2 Iodine Value

The iodine value of oil is a measure of its average level of unsaturation, and an index of the number of double bonds (capable of reaction with halogen) within it. Iodine

value is reported in terms of the grams of iodine that will react with 100 g of fat or oil under specified conditions.

Iodine value expresses the concentrations of the unsaturated fatty acids, together with the extent to which they are unsaturated, and is therefore a simple and very useful quality parameter during frying (Rossell 1983; Roth and Rock 1972). The iodine value tends to decrease with time because oil is used in the frying system. This decrease is indicative of the increased rate of oxidation during frying due to the consumption of double bonds by oxidation and polymerization (Abdel-Aal and Karara 1986; Alexander 1978; Chang, Peterson, and Ho 1978). However, the iodine value of the fresh oil must be known to determine the rate of change during frying (Lawson 1985).

Alim and Morton (1974) reported that the decrease in iodine value is a result of complex physicochemical changes. Oxidation reactions involve the double bond through chain reactions adjacent to the double bond to form VDPs, or by direct interaction across the bond to form 1,2 diols.

### 4.4.3 Fatty Acid Profile

Knowledge of the fatty acid composition of oil can relate possible oxidation with specific unsaturated fatty acids. Determination of the polyunsaturated fatty acid content (PUFA) of oil is the main index of its oxidative stability. Varela (1980) showed that highly unsaturated PUFAs, such as linolenic acid, are more readily oxidized and polymerized than less unsaturated ones. As the number of double bonds in a fatty acid increases, the relative rate of oxidation increases (Beckmann 1983). Linolenic acid, which contains three double bonds, is the most sensitive fatty acid to oxidation, whereas linoleic acid is less reactive. The frying stability of highly unsaturated vegetable oils (e.g., sunflower oil and soybean oil) can be improved by hydrogenation to reduce the level of linolenic acid and linoleic acid, and consequently to improve their oxidative and heat stabilities, as well as to eliminate fishy odors associated with linolenic acid (Razali and Bardi 2003).

Changes in the fatty acid profile of oils during frying are basically among the unsaturated fatty acids, whereas the saturated fatty acids (myristic, palmitic and stearic) are slightly increased (Tyagi and Vasishtha 1996). However, as indicated in many studies (Chatzilazarou et al. 2006; Tsaknis et al. 1999), the reduction of PUFA content may not be significant.

### 4.4.4 Conjugated Dienes

The method is based on the production of conjugated alkene bonds in the fatty acid chains, and their measurement in the ultraviolet region. The oxidation of polyunsaturated fatty acids during frying is accompanied by increased ultraviolet absorption. White (1991) reported that when polyunsaturated fatty acids are oxidized, a shift in one of the double bonds occurs, producing a conjugated diene that can be measured by ultraviolet absorption. When linoleic acid is oxidized to give linoleic acid hyperoxide and becomes conjugated, the conjugated compounds absorb near 232 nm, whereas the secondary diketones absorb at 268 nm, and the conjugated fatty acid trienes absorb near 268 nm, together with a secondary peak at 278 nm (Gray 1978). Jacini (1976) reported that $\alpha$-diketones and unsaturated $\alpha$-ketones absorb strongly at 270 nm. The magnitude of change is not readily related to the degree of oxidation,

but the changes in the ultraviolet spectrum of a given substance can be used as a relative measurement of oxidation (Gray 1978; White 1991).

Good correlations between conjugated dienes and peroxide value have been found (Evans et al. 1974; Robertson, Morrison, and Burdick 1973). However, the method has less specificity and sensitivity than measurement of peroxide value (Eiserich, Macku, and Shibamoto 1992). Carotenoids, which absorb in the same region, may affect the results (Maillard 1916). An alternative spectroscopic method measuring conjugable oxidation products has been proposed by Parr and Swoboda (1976), who showed that not only the fatty acid hydroperoxide, but also the hydroxy and carbonyl compounds derived from them, can be measured. They referred to them as "conjugable oxidation products" which are measured together and expressed as the "COP".

Ultraviolet absorption at 232 nm shows an almost constant increasing diene content with progress of heating time throughout the process (Tsaknis et al. 1998a; Tsaknis et al. 1999). However, the rate of increase in diene content in later stages of frying is expected to be lower, finally reaching a plateau, due to the establishment of an equilibrium between the rate of formation of conjugated dienes to that of polymers (Peled, Gutfinger, and Letan 1975) forming by a Diels–Alder reaction involving conjugated dienes. It is now generally accepted that thermal polymerization requires a conjugated double bond in one of the FFAs (Augustin and Berry 1983). This test is the most useful method for measuring heat abuse of polyunsaturated oils, but is less applicable to fats containing few unsaturated oils.

### 4.4.5 Rancimat Method

The Rancimat method, developed by Hadorn and Zürcher (1974), is based on the fact that the volatile acids formed during oxidation (De Man, Tie and De Man 1987; Loury 1972) can be used for automated endpoint detection.

Determination of oxidative stability with the Rancimat method features automatic plotting of conductivity against time. The evaluation is done graphically after completion of the experiment (Hudson 1983; Läubli and Bruttel 1986; Matthäus 1996).

Although most of the problems associated with accelerated methods of measurement of rancidity development (e.g., active oxygen method) also occur in the Rancimat technique, the latter has obvious advantages. It is simple to run. It measures oxidative products automatically, therefore all stages during the whole deterioration period of the oil are detected. Precision control of oxidation conditions allows accurate and reproducible results (Läubli and Bruttel 1986; Rossell 1983).

Induction period measurements are carried out on frying oils to provide quick indication of the trends in resistance to oxidative rancidity of the heated oils. The induction period determined via accelerated oxidation methods on the original oil cannot guarantee or predict the actual frying performance of the oil because other factors will be introduced once frying commences (e.g., badly operated fryer or heat exchanger will ruin even the best-quality oil). Nevertheless, it is considered that the Rancimat induction period can be useful to act as a "screening" test and eliminate the possibility of introducing lower-stability oils into the production area with all the attendant consequences (Morton and Chidley 1988).

### 4.4.6 Free Fatty Acid Content

FFA content is the most frequently used test (sometimes is the only one). Determination of FFA content appears to be the method favored for quality-control evaluation of frying oils. The FFA content is given as percent FFA (% FFA), calculated as oleic acid (but sometimes as percent palmitic acid for palm oil). Any acidic compound in the oil is included. Thus, citric acid, added to refined oil as a metal chelator, will increase the apparent FFA content. This possible complication must be considered if a sample appears to have excessive FFA (Stauffer 1996).

During frying, the steady rise in the formation of FFA can be attributed partly to the hydrolysis and partly to the component carboxylic groups present in polymeric products of frying (Tyagi and Vasishtha 1996). The acidity is mainly formed by hydrolysis of triglycerides, which is promoted by food moisture, and by oxidation or by the reaction of oil with moisture formed during other deterioration reactions (Al-Harbi and Al-Kabtani 1993).

Several factors should be considered when using this method. The level of FFA found in the frying oil not only reflects those formed during the frying process, but also the level of acidity initially formed in the oil before heating (Fritch 1981). In addition, FFAs are formed during frying by oxidation and hydrolysis. The rates of these processes vary according to a number of variables, including the type of vegetable oil being used and initial FFA levels. The rate of FFA production may also vary over time within the same operation. The methods used for FFA determination do not permit differentiation between FFA formed by hydrolysis and those formed by oxidation. Therefore, use of FFA alone to indicate when frying oil should be discarded can often result in "acceptable" oil being discarded and, in some cases, spent oil being retained for frying (Stevenson, Vaisey-Genser, and Eskin 1984).

### 4.4.7 Viscosity

Viscosity controls the amount of oil that coats the fried product as it leaves the fryer. It therefore has an important role in oil absorption and uptake of oxidized products by the fried food (Alim and Morton 1974). As the oxidation, accelerated by heat, proceeds, the viscosity progressively increases (Tyagi and Vasishtha 1996). Oxidation products include aldehydes, ketones, hydrocarbons and many polymeric compounds. The latter lead to changes in viscosity and heat-transfer efficiency of the oil. Formo (1979) and McGill (1980) reported that the rate of viscosity increase parallels the rate of polymer formation. Additionally, viscosity varies with temperature (Blumenthal 1996).

Linoleic acid and linolenic acid are extremely vulnerable to oxidation and also undergo thermal degradation to form polar and polymer compounds, resulting in increased viscosity of the frying oil (Razali and Bardi 2003).

Alim and Morton (1974) reported that the build-up of NVDPs causes an increase in viscosity. This increase is a result of formation of compounds with increased chain length. This increases the molecular cohesiveness; chain branching which shows its effect by increased molecular interference; polar groups which are formed as a result of oxidative changes affect the resistance to shear by providing greater binding forces through hydrogen bonding and dipole association; and formation of higher molecular

weight polar compounds (carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges) between fatty acids (Al-Habri and Al-Kabtani 1993).

### 4.4.8 Smoke Point

The smoke point is the temperature at which smoking is first detected in laboratory apparatus protected from drafts and provided with special illumination. The temperature at which the oil smokes freely is usually higher. The smoke point of vegetable oils is a measure of their thermal stability when heated in contact with air. FFAs and other volatile substances affect the smoke point. Determination of smoke point has little importance for fried oils, but can be considered an indicator of the temperature limit up to which oil can be heated.

Morton and Chidley (1988) reported that the amount of smoke emanating from a cup is directly proportional to the concentration of low molecular weight decomposition products in the oil. Roth and Rock (1972) reported that FFAs and other volatile substances leaving the oil as gases will not appear as a smoke until their concentration is sufficient to permit aggregation to colloidal-sized particles. The temperature (at which the requisite supersaturation of the air above the oil with gaseous molecules is reached) is decreased when the accumulation of products (particularly fatty acids and monoglycerides) of the oxidative and hydrolytic deterioration advances. The formation of oxidized triglycerides, partial glycerides, dimers and trimers lead to a lowering of the smoke point (Morton and Chidley 1988). The unsaturation of oil has little, if any, effect upon its smoke point (Formo 1979).

According to Stevenson, Vaisey-Genser, and Eskin (1984), the determination of smoke point through a standard procedure still relies heavily on the ability of the worker to determine the point at which the oil begins to smoke. White smoke over frying oils is mostly steam. Blue-to-gray smoke contains organics co-distilling with steam. This latter condition can indicate the oil is unfit for use, but cannot be used for quantification (Blumenthal 1996).

### 4.4.9 Polar Compounds and Polymers

If a moist food is placed in oil at frying temperatures, air and steam are involved and initiate a chain of interrelated reactions. The free radicals formed can also react to form polymers and other complex reaction products. Many of the above reactions are interrelated and a complex mixture of products is therefore formed, but non-volatile products can generally be classified as polar and/or polymeric compounds (Lumley 1988).

During the heating process, various chemical reactions result in the formation of compounds with high molecular weight and polarity. These compounds are non-volatile and steadily increase in concentration with heating time (Lumley 1988).

According to Billek, Cuhr, and Waibel (1978) and Paradis and Nawar (1981), polar compounds indicate the degradation of oils and the breakdown of triglycerides, mainly resulting in the formation of dimer triglycerides with a molecular weight of about 1800, and monoglycerides.

Polar compounds include all oxidized and dimerized triglycerides, FFAs, mono-glycerides and diglycerides, sterols, carotenoids, antioxidants, antifoamers, crystal inhibitors, bleaching earth, filteraid, hydrogenation catalyst residues, soaps, residues

of chlorophyll and phospholipids (Blumenthal 1996), and other materials soluble in, emulsified in, or suspended particulates in frying oil.

Many researchers consider measurement of polar materials to be the single and most important test for assessing degrading oil. Fritch (1981) reported that the analysis of percentage polar compounds is considered to be one of the most reliable indicators of the state of the oil deterioration. This latter statement is also supported by other research workers (Gere 1982). As indicated by Lalas and Dourtoglou (2003) and Romero, Cuesta, and Sanchez-Muniz (1999), several European countries have passed specific laws and regulations concerning culinary oil used in frying. Many countries have set a maximum level of polar compounds at 25%, while others have established a polar compound cut-off point between 20% and 27%. Billek, Cuhr, and Waibel (1978) stated that any heated oil with $\geq 27\%$ polar compounds should be discarded. Romero, Cuesta, and Sanchez-Muniz (1999) used three equations (linear, logarithmic and power) to estimate the number of frying operations before the critical quantity of polar compounds was reached during frying in oil with frequent replenishment with fresh oil at a quantity lost during operations. Logarithmic and power equations appeared to define the changes more accurately because polar compounds tended to stabilize after a certain number of frying operations. However, when no replenishment with fresh oil takes place during frying, the linear equation seems to be more adequate because polar compounds keep increasing until the end of frying (Tsaknis and Lalas 2002).

Polymers form one of the groups of polar compounds and, of those originating at the high temperatures of the frying process, they are the most representative (Benedito et al. 2007). Polyunsaturated fatty acids have a higher tendency to polymerization than monounsaturated fatty acids. The latter originate a higher proportion of oxidized monomers, which are the second most important group of polar compounds (Marquez-Ruiz, Tasioula-Margari and Dobarganes 1995).

Polymers include dimmers, trimers, and tetramers, and may be formed through oxidative and thermal reactions. The dark "shellacs" that form on fryer walls, heater tubes, and belts are polymeric (sometimes sticky) materials. They are an excellent chemical marker of oil degradation, but not applicable for monitoring food quality (Blumenthal 1996).

Two types of polymers are formed in fryer oil (Nawar 1985): oxidative and thermal polymers. Oxidative polymers are formed in autoxidation when free radicals terminate each other as under autoxidation. These oxidative polymers do not always impart an off-flavor to freshly fried food but, because they are strong free radicals, they can decompose during storage of the fried product. Thermal polymers can occur under heat with or without oxygen due to excessive fryer heat and excessive fryer down-time. Heat can cleave the oil molecule or fatty acid. These cleaved compounds can then react with each other, forming large molecules. They impart a bitter aftertaste to the fried food (Gupta 2005).

### 4.4.10 Color

Oil color has been used as a quality index. The color of vegetable oil changes markedly with its deterioration during frying. Darkening is attributed to unsaturated carbonyl compounds or non-polar compounds of foodstuff solubilized in

the oil (Gutierrez, Gonzalez, and Dobarganes 1988). Color change is a result of the diffusion of pigments into the oil during frying (Lalas, Gortzi, and Tsaknis 2006).

Artman (1969) reported that the increase of color content was attributed to the α -, β- unsaturated carbonyl compounds which are intermediates to resulting NVDPs containing carbonyl groups. Perkins (1967) and Stevenson, Vaisey-Genser, and Eskin (1984) showed that the formation and accumulation of NVDPs are responsible for physical changes in the frying oil such as increases in color. These products can absorb energy of the magnitude of visible light, and this ability is associated with certain unsaturated molecular groups that provide energy-absorbing resonance.

David, Sherman, and Stephen (1975) reported that minor constituents with molecular weight 300–551 and containing double bonds, carboxyl, ester, peroxide and hydroxyl groups, were effective in causing the darkening of oils during frying.

Carbonization and caramelization of food material during frying creates oil-soluble color bodies that transfer to the frying oil (McGill 1980; Roth and Rock 1972).

Many methods have been devised for the measurement of the color of vegetable oils such as the Wesson colorimeter technique, the Lovibond Tintometer, and the spectrophotometric index method. These represent an attempt to measure the color of vegetable oils on a scientific basis.

As indicated by Blumenthal (1996), red color loosely correlates to combined oxidized fatty acids and pyrolytic condensation products. Yellow color usually relates to combined peroxides and aldehydes, and is also related to carotenoids and other compounds. Blue color is related to the haze created by water and fine particulates suspended/emulsified/dispersed in the oil.

Burton (1989) reported that the α, and β-unsaturated carbonyl compounds, derived from sugars, are the first formed intermediates that react with substances containing α-amino groups to give carbonyl–nitrogen compounds which conjugate to form brown products (Maillard reaction). According to Lalas and Dourtoglou (2003), the color of fried products with high content of sugars (e.g., potato chips) is produced mainly by Maillard reactions. For example, the higher increase of oil color during potato frying than that during fish frying is due to the reactions in potatoes between the aldehyde group of sugar and amino acids, giving rise to brown products. Antioxidants not only reduce oxidation but also block (indirectly) the Maillard reaction via the inhibition of the final pyrazine formation phase (Porter et al. 2006), thereby reducing the darkening of fried foods.

### 4.4.11 Thiobarbituric Acid Test

Robards, Kerr, and Patsalides (1988) suggested that the TBA test was satisfactory for evaluating frying fat in the early stages of rancidity. The TBA test was perhaps the most widely used method for detecting lipid oxidation in foods. Although it is only an empirical assay, it has gained wide use because of its simplicity and sensitivity. The general procedure (of which there are numerous variants) involves heating a small quantity of oil for a defined time in an aqueous acidic solution of TBA, then measuring the absorbance at 532–535 nm of the red chromogen. This is formed through the condensation of two molecules of TBA with 1 molecule of malondialdehyde (MDA), a secondary product in the autoxidation of PUFAs.

Only peroxides that possess unsaturation, $\beta$, $\gamma$, to the peroxide group are capable of undergoing cyclization with the ultimate formation of MDA. Such peroxides can be produced only from fatty acids containing $\geq 3$ double bonds (Frankel 1984).

Other investigators suggested possible precursors of MDA to be bicyclic peroxides analogous to the prostaglandin endoperoxides (Pryor and Stanley 1975; Pryor, Stanley, and Blair 1976) or simply $\alpha$, and $\beta$ unsaturated aldehydes formed by decomposition of hydroperoxides.

MDA reacts with various compounds to form derivatives, which can be estimated from their absorption in the visible region. Other aldehydes also react with most of these compounds to form yellow or orange complexes which can interfere in the estimation of MDA if they are present in the sample and are not separated from the MDA complex (Draper and Hadley 1990).

Several workers have investigated high-performance liquid chromatography (HPLC) methods for the direct quantification of MDA in food products because the colorimetric determination of malondialdehyde is subject to interference. Tsaknis et al. (1998b) suggested an improved HPLC method for the quantification of MDA in vegetable oils at $1.5 \times 10^{-9}$mole/L.

### 4.4.12 Sensory Evaluation

Rancidity describes the unpleasant odors and acid flavors in food resulting from deterioration of fat. The ultimate assessment for rancidity must be by taste because it measures what the consumer perceives. As indicated previously, thermal polymers can be detected in the fresh product by expert panelists because they generally impart a bitter aftertaste to the fried food. Taste panels are time consuming and costly. Consequently, objective methods have been developed that can be correlated by statistical techniques with the sensory attributes of the food and as a result with the oil used for frying it. Sensory evaluation is currently capable of assessing the composite sensory attributes of a food fried in certain oil.

According to Gunstone and Norris (1983), the scoring test is commonly used in grading oils for quality (i.e., degree of rancidity or oxidative damage). The descriptive analysis, including detection and the description of the qualitative and quantitative sensory aspects of a product, is done by a trained panel because the sensitivity to the off-flavors varies between individuals (Pokorny 1989). The sensory induction period of the product can be determined (Shahidi and Zhong 2005).

### 4.4.13 Recent Methods

Many new methods have been proposed to estimate the quality of frying oil rapidly and with high sensitivity.

Using ultrasonic techniques, the quality of frying oils covering a wide range of oil degradation and degree of unsaturation can be analyzed. Lacey and Payne (1991) reported that ultrasonic methods can measure the change in viscosity of the oil. Benedito et al. (2002) and Benedito et al. (2007) suggested a method for ultrasonic assessment of oil quality during frying. Vijayan, Singh, and Slaughter (1993) reported correlations between viscosity and absorbance. Ultrasonic velocity

and viscosity could be used to characterize the thermal degradation of frying oils subjected to very different frying conditions. According to Benedito et al. (2007), velocity proved to be linearly related to viscosity and to the percentage of polar compounds and polymers. These relationships were dependent on the type of oil that was classified as monosaturated and polyunsaturated. Temperature of the ultrasonic measurements affects not only the accuracy, but also the goodness of the relationships between ultrasonic velocity and the percentage of polar compounds and polymers. The use of velocity and viscosity in a single prediction model allowed classification of 97.5% of oil samples correctly, according to the 25% polar compounds limit (Benedito et al. 2007). However, the particles contained in the oil should be previously removed to avoid any effect of the fried product on ultrasonic measurements.

Innawong, Mallikarjunan, and Irudayaraj (2001) investigated the possibility of using Fourier transform infrared (FTIR) spectroscopy to differentiate between varying intensities of oil rancidity, and to investigate the quality of frying oils. Later, Innawong et al. (2004) used the whole spectra from Fourier transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) to differentiate between good, marginal and unacceptable oils with regard to various intensities of oil rancidity. Additionally, Innawong, Mallikarjunan, and Marcy (2004) determined the quality of frying oil using a chemosensory system.

Kazemi et al. (2005) used visible/near-infrared hyper-spectral analysis to monitor the quality of frying oil. The authors found that the spectral reflectance of the oils can be used to effectively predict three quality parameters (acid value, total polar compounds, and viscosity). Partial least-squares calibration models using wavelengths of 400–1750 nm were selected to track the changes of the three parameters of the heated oil samples with high accuracy. The $R^2$ values for predicting the three quality parameters were 0.95 for acid value, 0.91 for viscosity, and 0.98 for total polar compounds. Authors suggested that the method could be used as a basis to design online oil-quality evaluation systems.

Greenwood (2007) exploited near infrared (NIR) spectroscopy to test the quality of frying oil. The method could satisfactorily determine, in $<2$ minutes, the polar materials contained in oil without harming the sample. Data were taken as direct transmission measurements over 1100–2500 nm using a Foss scanning spectrometer and NIR Systems software. The author developed calibration models using forward stepwise multiple linear regression and partial least-squares techniques.

Another method includes using a diode laser operating at 675 nm and a photodetector to measure transmittance of the oil *in situ* (United States Patent 1998) to continuously determine the quality of frying oil.

There are also fast techniques (“test kits”). These methods usually involve a calorimetric test comprising indicators which react with the oxidized compounds in a small quantity of frying oil in a disposable vial. The color developed is compared against a standard color, or by a colorimeter/spectrophotometer (values are converted to concentration units by reference to a chart). Test kits usually determine total polar materials, FFA and water emulsion titratables (soaps/moisture/surfactants). Other calorimetric tests are available, but the main drawback to these methods is that they measure only one aspect of oil quality (United States Patent 1998).

Other rapid tests, based on the physical properties of oil, measure changes in the dielectric constant (“food oil sensor” (FOS)). In the last years, efforts have been made in developing instruments which can measure the increase in viscosity and density occurring in parallel to oil degradation (Marmesat et al. 2007).

The rapid tests and test kits mentioned above are simpler and more rapid than the official methods, and are necessary to measure oil quality in restaurants and fried-food outlets. However, rapid tests are not used widely probably because they are expensive for quality control in small fryers (Marmesat et al. 2007).

## 4.5 ANTIOXIDANTS

The inhibition of oxidation of not only the fried oil, but also the oil absorbed by food, is very important. Absorbed oil continues to be oxidized even when the fried food is packed under nitrogen, leading to an unacceptable product.

Phenolic antioxidants are substances that can react with the initiating and propagating radicals to give harmless products and to extend the shelf-life of the substrate until autoxidation finally takes place (Sherwin 1972). Compounds that retard the rate of autoxidation of lipids by processes other than that of interrupting the autoxidation chain by converting free radicals to more stable species are termed “secondary antioxidants”.

Lipid peroxidation, which involves a series of free radical-mediated chain reaction processes, is also associated with several types of biological damage. The role of free radicals and active oxygen is becoming increasingly recognized as the cause of the atherogenesis in humans (Kishk and Al-Sayed 2007). This helps to justify antioxidants that can reduce or retard deterioration of frying oil. Additionally, antioxidants minimize discoloration, and off-flavor, and contribute in emulsion stability that can be negatively affected by the degradation of oil (Kishk and Al-Sayed 2007; Mitsumoto et al. 2005).

Synthetic antioxidants are not popular among consumers because they have been demonstrated to be promoters of carcinogenesis, mutagenesis (Farag et al. 1989) and other undesirable effects. Natural antioxidants have been recognized as presenting varying levels of antioxidant activity (Che Man and Tan 1999; Kim et al. 1994; Zhang et al. 1990). Some of the commonest natural antioxidants are tocopherols, sterols, and flavonoids from plant extracts.

Tocopherols occur as minor constituents in all vegetable oils. They are among the best known and most widely used antioxidants. Their antioxidant activity largely depends on the substrate to which they are added, temperature, availability of oxygen and light, and the presence of transition metals and various synergists. The amounts and the types of tocopherols vary with oil type. The commonest types in seed oils are $\alpha$-, $\gamma$-, and $\delta$-tocopherols. These compounds protect the oil from oxidation during processing, storage, transportation, and, also, later in the fryer (Gupta 2005).

The greater stability of vegetable oils compared with animal fats under oxidative conditions is known to be due to the higher levels of natural antioxidants (tocopherols) in the oils (Carpenter 1979).

There is a disagreement in the order of antioxidant activity of tocopherols. Bourgeois and Czornomaz (1982) and Von Pongracz, Hoffmann-La Roche, and Basel

(1984) reported the decreasing order of antioxidant activity of tocopherol as $\delta > \gamma > \alpha > \beta$ at 80–120°C; and as $\alpha > \gamma > \beta > \delta$ at 20–60°C. Conversely, according to Parkhurst, Skinnar, and Sturm (1968), the antioxidant activity of tocopherol was in the decreasing order of $\gamma > \delta > \beta > \alpha$, whereas it was $\alpha > \beta > \gamma > \delta$ in the study of Burton and Ingold (1981). Sonntag (1979) reported that the decomposition rate of $\gamma$-tocopherol was greater than that of $\alpha$-tocopherol after 10 hours of frying. Lea (1960) showed that the order of antioxidant activity changed with the oil used for the experiment. In contrast, Miyagawa, Hirai, and Takezoe (1991), using a mixture of soybean and rapeseed oils to fry potatoes, found that the order of decomposition rates of tocopherols were $\gamma > \delta > \alpha$ after 32 batches of frying. Carlson and Tabach (1986) also reported the same decomposition rates in soybean oil used for frying French fries. Zero values of $\delta$- and $\gamma$-tocopherols were also observed. These were possibly present in oils but could not be detected because their concentration was much below the limit of detection of the method used (1 mg/kg).

As indicated by Gupta (2005), freshly refined oil may contain tocopherols at concentrations lower than the desired level. In such cases, supplementing the oil with $\gamma$- and $\delta$-tocopherols, or $\gamma$- and $\delta$-tocotrienols, can significantly improve oxidative stability of the oil. However, the cost of the operation is increased.

Sterols are 27–29-carbon compounds that occur at low levels in vegetable oils and fats. The composition of the sterols in oil enables one to distinguish vegetable oils from animal fats or fish oils because vegetable products contain only very low levels of the sterol cholesterol (Rossell 1991). Knowledge of the sterol composition of oil can not only provide information about the identity of this oil, but also relate possible resistance to oxidation with specific sterols such as $D^5$-avenasterol. Gordon (1990) reported that although most sterols are ineffective as antioxidants, $D^5$-avenasterol, fucosterol and citrostadienol have been shown to exhibit antioxidant properties in oils heated to $> 180$°C. It has been suggested that the donation of a hydrogen atom from the allylic methyl group in the side chain, followed by the isomerization to a relatively stable tertiary allylic free radical represents the mode of action of sterol antioxidants. $D^5$-avenasterol appears to be increased in concentration in a layer at the surface, and it is ineffective at room temperature. These findings suggest that avenasterol acts as an antioxidant, with its effectiveness arising from its concentration on the surface, where oxidation occurs. Sims, Fioriti, and Kanuk (1972) reported that vernosterol and $D^7$-avenasterol have considerable inhibitory activity.

A common practice to retard the deterioration of heated oil is the addition of antioxidants and/or anti-polymerization agents (Kalantzakis and Blekas 2006). Extracts of many plants have been shown to have various degrees of antioxidant activity in different fats and oils (Dewdney and Meara 1977; Pokorny, Yanishlieva, and Gordon 2001). The isolation of natural antioxidant agents from natural sources and their use as antioxidants can satisfy the consumer preference for natural products and also be economically viable. Some of these natural products are derived from the plants of the *Lamiaceae* family, such as rosemary, sage, oregano and summer savory (Kalantzakis and Blekas 2006).

Many studies concerning the use of natural antioxidants during frying to retain the quality of oil and food have been completed. Kalantzakis and Blekas (2006) studied the effect of extracts obtained from Greek sage and summer savory on the

thermal stability of vegetable oils heated at frying temperature. Bensmira et al. (2007) proved the effect of lavender and thyme incorporated in sunflower seed oil on its resistance to frying temperatures. Lalas and Dourtoglou (2003) determined the effect of a natural plant extract, dissolved in frying oil, against oil oxidation, during intermittent frying of potato chips. The extract inhibited the oxidation of the frying oil, but also reduced the intensity of color of the fried product.

## 4.6 CONCLUSIONS

Deep-fried foods are becoming increasingly popular all over the world. With the goal being to produce high-quality food, the processor or foodservice operator should strive to keep frying oil at the top or optimal part of the quality curve for as long as possible (Blumenthal 1996). However, it is difficult to estimate the effects of each factor, and to keep the fryer at conditions that maintain the optimal concentration of deterioration products to assure the maintenance of good flavor and other characteristics with good shelf-life (Gertz 2000).

The determination of quality parameters of the oil used for frying and the optimization of the frying operation are crucial because improper monitoring of oil discard times makes producing fried foods of good quality impossible. Several physical and chemical characteristics of a frying oil that are used to determine its quality aspects were described. These parameters are indicators of the state of oil deterioration, but none of them can adequately judge frying life in all situations.

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# 5 Kinetics of Quality Changes During Frying

*Franco Pedreschi and Rommy N. Zúñiga*

## CONTENTS



## 5.1 INTRODUCTION

Frying is one of the oldest processes of food preparation. For decades, consumers have desired fried foods because of their unique combination of flavor and texture. The quality of the products from frying depends not only on the frying conditions, but also on the type of oils and foods used during the process (Aguilera 1997; Aguilera and Gloria-Hernández 1997).

Deep-fat frying is a widely used food process. It consists of immersion of food pieces in hot vegetable oil. Potato is the raw food material that has been used most in frying operations due to the high demand of consumers all over the world. For potato frying, the oil temperatures can be 120–190°C, but the commonest temperatures are 170–190°C (Pedreschi et al. 2005b). High temperature causes partial evaporation of water, which moves away from the food and through the surrounding oil, and a certain amount of oil is absorbed by the food. The final oil and moisture content of French fries are almost 15 and 38%, respectively (Aguilera and Gloria-Hernández 2000; Saguy and Dana 2003). Potato chips are very thin pieces (thickness, 1.27–1.78 mm)

of potatoes fried to a final oil and moisture content of ~35 and 1.7%, respectively (Moreira, Castell-Perez, and Barrufet 1999). French fries represent a composite structure formed by two regions: (i) an external dehydrated and crispy region where oil is located; and (ii) a humid and cooked core free of oil. The external crust is very similar to the structure of a fried potato slice or potato chip (Pedreschi and Aguilera 2002; Pedreschi, Aguilera, and Pyle 2001).

The term "quality" comprises several parameters of the frying material, either in mid-state (at intermediate stages of the frying process) or after completion of frying (Krokida et al. 2001b). The properties that determine the overall quality in food frying are moisture content, color, textural properties, structure, oil content and nutritional value. Recently, acrylamide has been classified as a potential carcinogen in humans (Rosen and Hellenäs 2002; Tareke et al. 2002). Frying processes provide ideal conditions for acrylamide formation because formation takes place only at temperatures > 100°C (Becalski et al. 2003; Mathaüs, Haase, and Vosmann 2004). This chapter considers acrylamide content as another quality parameter because it is closely related to food safety and nutritional issues.

Kinetic studies of quality changes during frying are the great importance because knowledge on kinetic parameters during the process enables prediction of final quality changes and improves the final product value through correct selection of frying conditions. The rate of change can be correlated with product (or composition) factors and/or environmental factors. The composition factors are related to the nature of food such as the properties of individual components, concentration, moisture content, water activity and pH. The main environmental factors are temperature, time and pressure (Hindra and Baik 2006).

For the last 11 years, kinetic studies of quality changes during frying have been focused on potato products. The study and modeling of the kinetics of changes in some important physical properties in potatoes during frying has been made by some researchers (Gupta, Shivhare, and Bawa 2000; Krokida et al. 2001b; Moyano and Berna 2002; Moyano, Rioseco, and Gonzaléz 2002; Moyano and Pedreschi 2006; Pedreschi, Aguilera, and Pyle 2001; Pedreschi and Moyano 2005a; Pedreschi et al. 2005a; Sahin 2000). However, there are studies in many other products such as meatballs, tofu, tortilla chips, chicken nuggets, pork meat and donuts (Ateba and Mittal 1994; Baik and Mittal 2003; Moreira, Sun, and Chen 1997; Ngadi, Li, and Oluka 2007; Sosa-Morales, Orzuna-Espíritu, and Vélez-Ruiz 2006; Vélez-Ruiz and Sosa-Morales 2003). Researchers have expressed the variation of quality during frying using empirical models (57%) or theoretical kinetic models (43%) (Hindra and Baik 2006).

This chapter reviews the kinetics of quality changes during deep-fat frying mainly of potato products. It focuses on the effect of different pretreatments to improve the quality parameters of the final products.

## 5.2 MOISTURE CONTENT

Moisture content is an important property in the quality of fried food products. The moisture content of fried foods denotes the quantity of water per unit mass of wet or dry product, and is usually expressed as a percentage (Moreira, Castell-Perez, and Barrufet 1999).

Deep-fat frying, which can also be defined as a process of drying, may be classified into four stages: (i) initial heating; (ii) surface boiling; (iii) falling rate; and (iv) bubble end point (Farkas 1994). Initial heating is described as the immersion of a raw material into hot oil and is characterized by the absence of water vaporization. During this stage, heat is transferred from the oil into the food by free convection and through the food by conduction. Surface boiling is characterized by the sudden loss of free moisture at the surface, increased rate of surface heat transfer, and inception of crust formation. The falling rate stage parallels that of drying, in which there is continued thickening of the crust region, decreased heat transfer rate and a steady decrease in the rate of vapor mass transfer from the potato sample. Bubble end point is characterized by the apparent cessation of moisture loss from the food during frying.

Moisture loss during frying generally decreases exponentially with frying time. Frying in hot oil at temperatures between 160°C and 180°C is characterized by a very high rate of drying. Moisture content of potato chips decreases from about 80% to $<2\%$ (wet basis (w.b.)) when they are fried. The mechanism of water loss during frying is complex, and the transport by molecular diffusion, capillary and pressure-driven flow should be accounted for. However, modeling at different levels of complexity has been reported. A first-order kinetics model in which the rate of moisture loss was proportional to the moisture content has been considered (Gupta, Shivhare, and Bawa 2000; Krokida et al. 2001b). In more complex models, the crust and core have been treated as two regions separated by a moving boundary and a pressure-driven flow in the crust region has been included (Farkas, Singh, and Rumsey 1996a, 1996b). With different approaches, Fick's law of diffusion (Equation 5.1) has been extensively used to describe the kinetics of water loss during frying in a slab of infinite extent (Kozempel, Tomasula, and Craig 1991; Moyano and Berna 2002; Pedreschi et al. 2005b; Rice and Gamble 1989; Williams and Mittal 1999).

$$MR = \frac{m_t - m_e}{m_0 - m_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left\{ \frac{1}{(2n+1)^2} \left[ \exp\left( -\frac{(2n+1)^2 \pi^2}{4} \frac{D_{\text{eff}} t}{l^2} \right) \right] \right\} \quad (5.1)$$

where $MR$ = moisture ratio; $m_t$ = moisture content at time $t$, dry basis; $m_0$ = initial moisture content, dry basis; $m_e$ = equilibrium moisture content, dry basis; $l$ = half-thickness of slab; $t$ = frying time; and $D_{\text{eff}}$ = effective moisture diffusion coefficient, assumed to be constant during the frying process.

For potato chips, the diameter is considerably larger than the width. It is therefore assumed that mass transfer takes place only in the axial direction. For the geometric shape of French fries, the superposition principle is used, i.e., the product of the solutions of the one-dimensional geometries, each of them having as a characteristic dimension of the length, the width and the height of the potato strip obtained from Equation 5.1, is taken. It is reasonable to assume that moisture content is negligible when equilibrium is reached in the frying process, i.e., $m_e = 0$ in Equation 5.1.

Moisture loss was expected to show a classical drying profile for different temperatures used in the frying process (Figure 5.1). As the temperature of frying increases, the moisture content for the same frying time decreases (Gupta, Shivhare, and Bawa 2000; Krokida et al. 2001b; Pedreschi et al. 2005a; Pedreschi et al. 2007d).

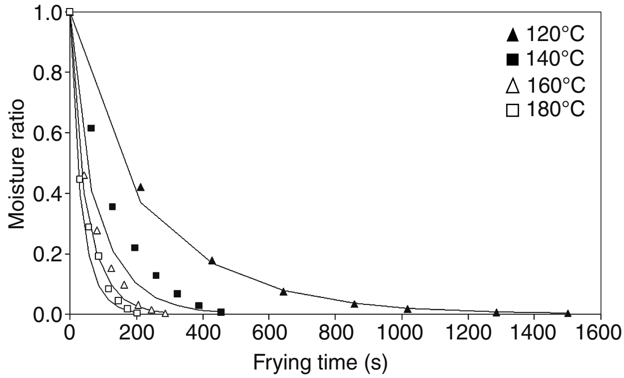



**FIGURE 5.1** Effect of frying temperature on moisture loss of potato slices. Experimental data and predicted by model Equation 5.1.

As expected, effective moisture diffusivity increased with frying temperature for potato strips and slices (Table 5.1). The same trend has been shown for tofu, chicken and pork meat (Baik and Mittal 2005; Kasama and Ngadi 2005; Sosa-Morales, Orzuna-Espíritu, and Vélez-Ruiz 2006).

For potato chips, blanching could cause partial starch gelatinization, originating a different microstructure with respect to control samples. However, no significant difference in water migration pattern was observed between raw and blanched samples (Pedreschi et al. 2005a).

For potato strips $D_{eff}$ values (obtained from Equation 5.1) of control potato were lower than that for impregnated potato (sucrose-NaCl solution, 15 min, 25°C) at all frying temperatures tested (Moyano and Berna 2002). The authors explain that control potato had 15% more oil, which acted as an additional surface resistance for water loss. The hydrophobic characteristic of fat imposes a resistance to the flow of water and can explain the decrease in $D_{eff}$ for control potato. Although soa king treatment in NaCl solution changes the surface properties of potato chips, moisture loss showed similar patterns in blanched and blanched and soaked chips because they have similar surface and internal microstructure (Pedreschi et al. 2007c, 2007d).

## 5.3 COLOR

Among the different classes of physical properties of foods and foodstuffs, color is considered the most important visual attribute in the perception of product quality. The aspect and color of the food surface is the first quality parameter evaluated by consumers and is critical in the acceptance of the product, even before it enters the mouth. Consumers tend to associate color with flavor, safety, storage time, nutrition and level of satisfaction because it correlates well with physical, chemical and sensorial evaluations of food quality (Pedreschi et al. 2006).

The determination of color can be carried out by visual, instrumental and computer vision (CV) methods. Visual observations may be unsatisfactory due to eye fatigue, poor color memory of subjects, lack of uniform lighting, lack of standardized viewing conditions, and non-availability of trained judges, especially for

**TABLE 5.1**
**Effective Diffusivity Coefficient[a] ($D_{eff}$) for the Constant Diffusivity Model**

| Product | Treatment | Temperature (°C) | | | Reference |
|---|---|---|---|---|---|
| | | **160** | **170** | **180** | |
| Potato strips | Blanched | 4.14 | 5.24 | 6.71 | Moyano and Berna (2002) |
| | Blanched and soaked in NaCl | 5.19 | 6.82 | 9.40 | |
| | | **120** | **150** | **180** | |
| Potato slices | Control | 3.86 | 9.86 | 17.2 | Pedreschi et al. (2005b) |
| | Blanched | 3.55 | 9.76 | 17.1 | |
| | Blanched and dried | 4.53 | 12.8 | 34.8 | |
| | | **140** | **160** | **180** | |
| Potato slices | Blanched | 9.94 | 15.2 | 21.3 | Unpublished results |
| | Blanched and soaked in NaCl | 10.1 | 14.5 | 20.5 | |

[a] Values of effective diffusivity in $m^2/s$.

routine large-scale determination of color quality (Hutchings 1994). Instrumental measurement of color of food products has often been done using colorimeters and spectrophotometers. Tristimulus colorimeters employ filters to convert the energy of the light reflected or transmitted through the sample into X, Y and Z values that locate the color of the sample in three-dimensional color space (Balaban and Odabasi 2006). CV involves acquisition and analysis of an image of a real scene by computers to obtain information or to control processes (Brosnan and Sun 2004).

### 5.3.1 Visual Measure of Color

Although human inspection is quite robust even during changes in illumination, determination of color is subjective and extremely variable between observers. Color standards or color charts are often used as reference material to permit a more objective color analysis (Figure 5.2). Unfortunately, their use implies a slower inspection and requires more specialized training of the observers. Hence, determining color through color-measuring instrumentation is recommended.

### 5.3.2 Instrumental Measurement of Color

In defining and quantifying color, a color system must be selected, usually among four alternatives: $L^* a^* b^*$, red, green and blue (RGB), XYZ and cyan, magenta, yellow and black (CMYK). Color of fried potatoes has been measured usually in units $L^* a^* b^*$ using a colorimeter or specific data acquisition and image processing systems (Moyano, Rioseco, and Gonzaléz 2002; Pedreschi et al. 2006; Santis et al. 2007; Segnini, Dejmek, and Öste 1999a). $L^* a^* b^*$ is an international standard for color measurements, adopted by the Commission Internationale d'Eclairage (CIE) in 1976. This color model creates a consistent color regardless of the device used to generate the image (e.g., monitor, printer or scanner). $L^*$ is the luminance or lightness

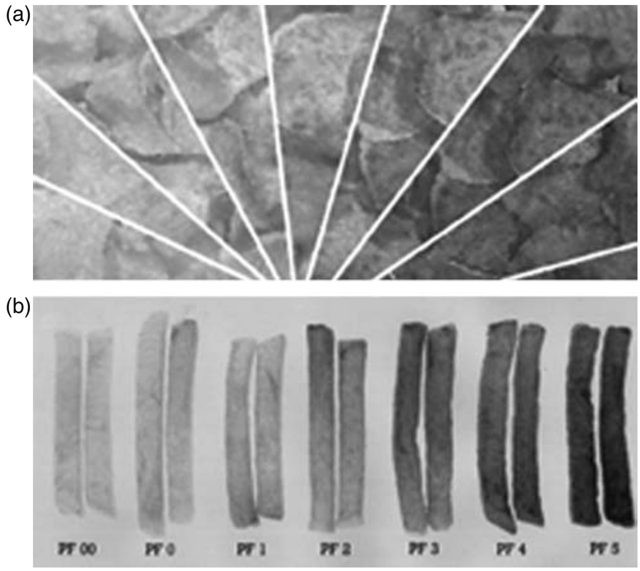



**FIGURE 5.2** Color charts for visual classification of fried potatoes. (a) Potato chips, (b) potato strips.

component, which ranges from 0 to 100, and parameters $a^*$ (from green to red) and $b^*$ (from blue to yellow) are the two chromatic components, which range from –120 to 120 (Papadakis et al. 2000). In contrast with other color models such as RGB and XYZ, color perception is uniform in the $L^* a^* b^*$ space. This means that the Euclidean distance between two colors corresponds approximately to the color difference perceived by the human eye (Hunt 1991).

Colorimeters such as Minolta Chroma Meter and HunterLab Colorimeter are commonly used for color measurement. They allow accurate and reproducible measurement of color. However, these instruments have the disadvantage that the surface to be measured must be uniform and small ($\sim$2 cm$^2$). They also provide a single average value for each measurement, which makes measurements quite unrepresentative and global analysis of the food surface more difficult (Mendoza and Aguilera 2004; Papadakis et al. 2000; Segnini, Dejmek, and Öste 1999a). Point-by-point measurements at many locations on the food sample must be made to obtain a color profile (Segnini, Dejmek, and Öste 1999a).

### 5.3.3 Measurement of Color by Computer Vision (CV) Systems

A CV system (Figure 5.3) consists of a digital or video camera connected to a computer for image acquisition, standard setting illuminants (usually a light box) and computer software for image processing and analysis (Balaban and Odabasi 2006; Brosnan and Sun 2004; Papadakis et al. 2000). CV analysis is a non-destructive method to objectively measure color patterns in non-uniformly colored surfaces and to determine other physical features such as image texture, morphological elements and defects (Mendoza and Aguilera 2004; Pedreschi et al. 2004). In recent years, CV

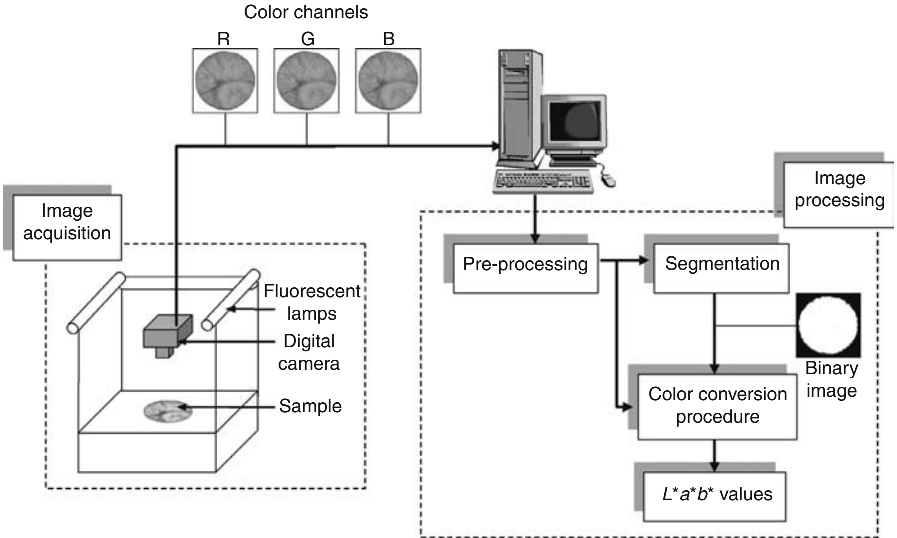



**FIGURE 5.3** Color vision system and steps required for the acquisition and digital processing of potato images.

has been used to measure objectively the color of fried potatoes because it provides some obvious advantages over a conventional colorimeter, i.e., analyzing the entire surface of the sample, and quantifying characteristics such as brown spots and other defects (Figure 5.4).

### 5.3.4 Color Kinetics

Color development in fried potatoes begins only if a sufficient amount of drying has occurred, and depends on the drying rate and the heat transfer coefficient during different stages of frying. Process variables such as time, oil temperature, and pretreatments of the raw materials are expected to affect the color of the fried products. Color changes in fried potatoes is the result of the Maillard reaction, which depends on the content of reducing sugars (mainly D-glucose) and amino acids or proteins at the surface, surface temperature, and frying time (Márquez and Añon 1986). At temperatures $< 60°C$, browning is normally a zero-order reaction. At higher temperatures, a plot of brown pigment versus time will curve upwards as in a first-order reaction (Hutchings 1994). A first-order kinetics analysis for browning during frying is expected because a deep-fat frying process usually has a very short period with a surface temperature $< 60°C$ (Moyano, Rioseco, and Gonzaléz 2002).

Many studies correlated color changes with frying temperature (oil temperature) and frying time (Krokida et al. 2001a, 2001b; Ngadi, Li, and Oluka 2007; Sahin 2000; Vélez-Ruiz and Sosa-Morales 2003). Only a few studies reflected the temperature of product surface into color kinetics (Baik and Mittal 2003; Moyano, Rioseco, and Gonzaléz 2002; Pedreschi et al. 2005a). The surface temperature of the potato (rather than the oil temperature set point or center temperature) should be considered because color development is a surface phenomenon.

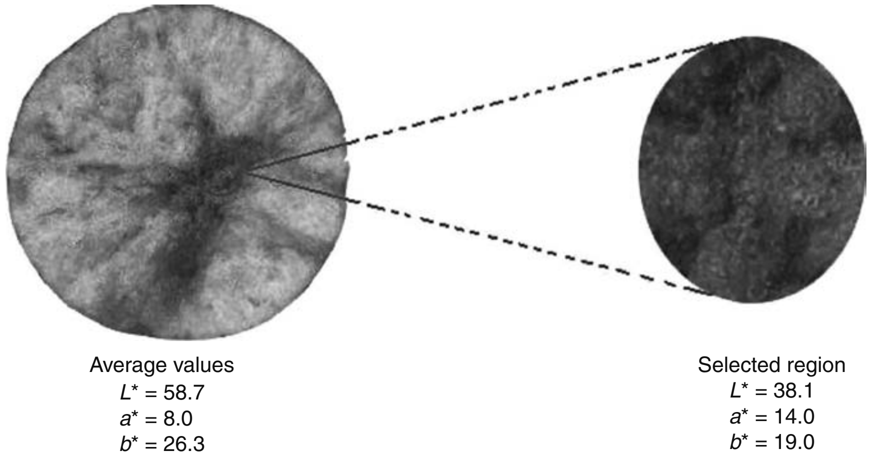



**FIGURE 5.4** Average color of potato chip and average color of a selected region in $L^*a^*b^*$ units. (From Pedreschi, F., León, J., Mery, D., and Moyano, P., *Food Research International,* 39. Implementation of a computer vision system to measure the color of potato chips, 1092–1098, copyright © 2006, with permission from Elsevier).

Some studies on color kinetics have been done by using a dynamic method originally proposed by Mizrahi and Karel (1978). This method uses the continuous change in moisture content and temperature to evaluate the kinetics of deterioration in moisture-sensitive products. It can be applied to cases where the reaction has a known order and is dependent on water content and temperature. The dynamic method requires moisture content, food temperature and deteriorative index (e.g., total color change, $\Delta E$) as a function of time. The procedure to obtain color kinetics parameters by the dynamic method is as follows: for a given value of moisture content and for each frying temperature, the time to reach that moisture and the corresponding surface temperature, $T_s$ are obtained (Figure 5.5a,b). Experimental data of mean moisture content, $m$, and surface temperature, $T_s$, fit to the following empirical relationships:

$$m = \left(m_0^{(1-n)} + (1-n)qt\right)^{\frac{1}{(1-n)}} \tag{5.2}$$

$$T_S = \frac{a_1 + a_2 t}{1 + a_3 t} \tag{5.3}$$

where $m_0$ is the initial moisture content, dry basis, $t$ is the frying time and $a_1$ to $a_3$, $n$ and $q$ are adjustable parameters obtained by multiple regression.

Color change during frying, $\Delta E$, fits to the following empirical relationship (Figure 5.5c):

$$\Delta E = b_1 + b_2 \exp\left(\frac{-t}{b_3}\right) \tag{5.4}$$

where, $b_1$ to $b_3$ are parameters of the model.

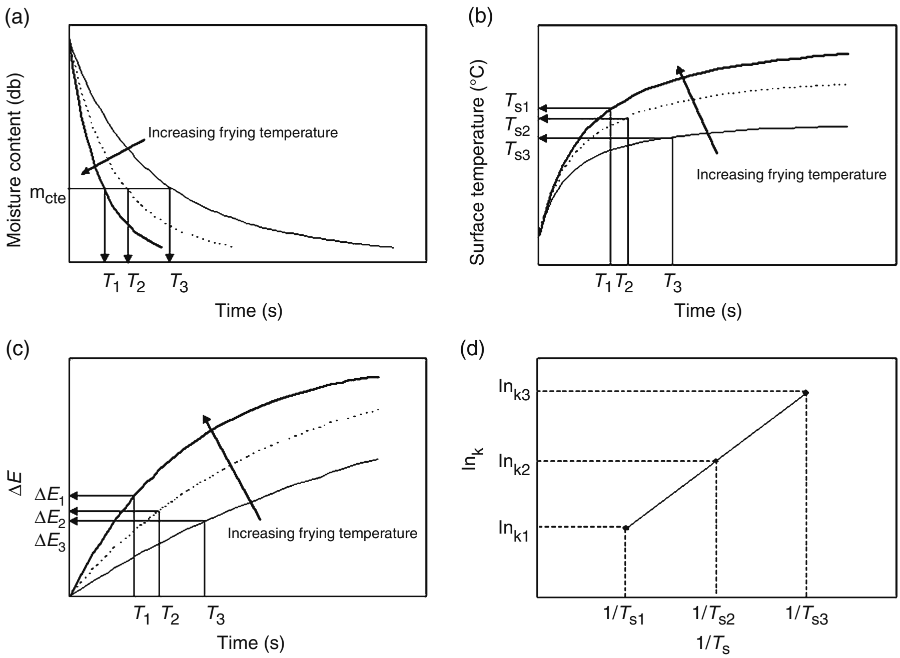



**FIGURE 5.5** Schematic explanation of the dynamic method.

From Equation 5.4, the rate of color change is calculated as:

$$\frac{d\Delta E}{dt} = \frac{-b_2}{b_3}\exp\left(\frac{-t}{b_3}\right) \tag{5.5}$$

To obtain the specific reaction rate of color change, $k$, the approach used by Ateba and Mittal (1994) is utilized. They calculated the rate of crust color change in meatballs by using first-order kinetics:

$$\frac{d\Delta E}{dt} = k\left(\Delta E_{max} - \Delta E\right) \tag{5.6}$$

where $\Delta E_{max}$ is the maximum total color change, determined experimentally for long times of frying.

In this way, $k$ is given by:

$$k = \frac{-b_2\exp\left(-t/b_3\right)}{b_3\left(\Delta E_{max} - \Delta E\right)} \tag{5.7}$$

Thus, at a given moisture content and their respective $T$s and reaction time, it is possible to determine the rate of color change and its specific reaction rate, $k$, from data of $\Delta E$ versus time. For a given moisture content, at each frying temperature,

different values for $T$s and $k$ are obtained, making it possible to draw an Arrhenius plot (Figure 5.5d) to determine the activation energy $E_a$ and the frequency factor $k_0$ from Equation 5.8. Table 5.2 shows activation energy values for potato products obtained by the dynamic method (as well as others works on this area).

$$\ln k = \ln k_0 + \frac{E_a}{RT_s} \tag{5.8}$$

Moyano, Rioseco, and Gonzaléz (2002) found that the activation energy for color change in the crust of French fries was a strong function of the potato moisture content during frying, decreasing from 151.8 kJ/mol at a moisture content of 1.4% (d.b.) at the beginning of the frying process to 49.1 kJ/mol at a moisture content of 0.3% (d.b.) towards the end. The mentioned activation energy values suggest a possible color development rate control from a chemical step (high values) to a diffusional step (low values). An enthalpy–entropy compensation study was done by Moyano and Zúñiga (2004) to clarify this point. It was found that enthalpy–entropy compensation occurs for browning of potato strips during deep-fat frying, with an isokinetic temperature of 333.1 K, and the browning mechanism reaction is controlled by entropy. It was shown that only one mechanism is present for browning during frying, and that the impregnation of the strips with the studied solutes had no effect on reaction mechanism.

**TABLE 5.2**
**Activation Energies of Color Parameters for Fried Potatoes**

| Product | Frying Conditions | Parameter | $E_A$ (kJ/mol) | Reference |
|---|---|---|---|---|
| Potato | Temperature, 180°C | $L^*$ | 129.7 | Marquez and Añon (1986) |
| Potato slices | Temperature, 150–180°C | $L^*$<br>$b^*$ | 94.85<br>71.67 | Sahin (2000) |
| Potato | Temperature, 160–190°C | $L^*$<br>$b^*$<br>$b^*$<br>$\Delta E$ | 89.9<br>55.9<br>34.8<br>59.3 | Nourian and Ramaswamy (2003) |
| French fries | Temperature, 160–180°C<br>Moisture content, 1.4–0.3 db | $\Delta E$[a] | Control, 151.8–49.1<br>Soaked NaCl, 174.6–55.9<br>Soaked corn syrup/NaCl, 102.7–44.4 | Moyano, Rioseco, and Gonzaléz (2002) |
| Potato chips | Temperature, 120–180°C<br>Moisture content, 1.6–0.8 db | $a^*$[a] | Control, 142.2–62.2<br>Blanched, 200.2–90.4 | Pedreschi et al. (2005a) |
| Potato chips | Temperature, 120–180°C<br>Moisture content, 1.6–0.8 db | $\Delta E$[a] | Control, 176.6–60.8<br>Soaked NaCl, 96.6–50.3 | Pedreschi et al. (2007c) |

[a] Obtained by the dynamic method.

### 5.3.5 Effect of Temperature and Pretreatments on Color Kinetics

Luminosity color component ($L^*$), which ranges from 0 to 100, decreases with increasing frying temperature and time because the potato slices get darker (Figure 5.6a). The higher the frying temperature, the darker the potato slices because non-enzymatic browning reactions are highly temperature dependant. A similar trend for $L^*$ for frying of potato strips and potato slices has been found (Bunger, Moyano, and Ríoseco 2003; Sahin 2000). The decrease in luminosity ($L^*$) during deep-fat frying is a typical change, and it has been reported for other fried products such as tofu, chicken nuggets, pork meat and donuts (Baik and Mittal 2003; Ngadi, Li, and Oluka 2007; Sosa-Morales, Orzuna-Espíritu, and Vélez-Ruiz 2006; Vélez-Ruiz and Sosa-Morales 2003). However, Krokida et al. (2001b) reported that the lightness of potato strips increases during the early stages of frying, whereas it remains almost constant afterwards. Some authors have modeled color changes of different foods during frying using first-order reaction kinetics. They showed that $L^*$ decreased exponentially with frying time and that the temperature dependence of the reaction rate constant was expressed using the Arrhenius relationship (Baik and Mittal 2003; Ngadi, Li, and Oluka 2007; Vélez-Ruiz and Sosa-Morales 2003).

The chromatic color component $a^*$, which ranges from –120 to 120, increases with frying time and frying temperature as a result of the formation of compounds from the Maillard non-enzymatic reaction. The chromatic component $b^*$ increases with frying time and shows the same trend of $a^*$; their values tend to increase faster as the frying temperature increases (Figure 5.6b,c). These results suggest that the redness and yellowness of potato slices increases during frying, and are coincident with those obtained by other researchers for potato chips and French fries (Krokida et al. 2001b; Pedreschi et al. 2007b; Sahin 2000). The same increase in redness ($a^*$) has been reported for other fried products, whereas the behavior of $b^*$ with frying time is unique for each product (Baik and Mittal 2003; Ngadi, Li, and Oluka 2007; Sosa-Morales, Orzuna-Espíritu, and Vélez-Ruiz 2006; Vélez-Ruiz and Sosa-Morales 2003).

The production of lighter color chips acceptable to the market often requires some pretreatment of the sliced potatoes in the processing plant (Krokida et al. 2001b). It is known that the blanching step before frying in potato chip processing improves their color (Califano and Calvelo 1987). Some potato processing plants use blanching prior to frying to improve the color of the chips because blanching could leach out reducing sugars from the potato tissue, leading to lighter color and avoiding an undesirable dark color in the potato slices after frying (Andersson 1994). Blanching reduces the $a^*$ values of fried potatoes, thus reducing $\Delta E$ values (Figure 5.7). This is probably due to the leaching out of reducing sugars before frying, inhibiting non-enzymatic browning reactions and leading to lighter and less red fried potatoes.

A simple way to change the surface properties of potato strips is by soaking them in a suitable solution, prior to frying, for an appropriate period of time. For the osmotic dehydration of potatoes, solute impregnation onto the surface is more important than water loss before frying (Bunger, Moyano, and Ríoseco 2003; Moyano and Berna 2002). Soaking in NaCl improved the color of potato chips because the values of $\Delta E$ diminished considerably with respect to those corresponding to

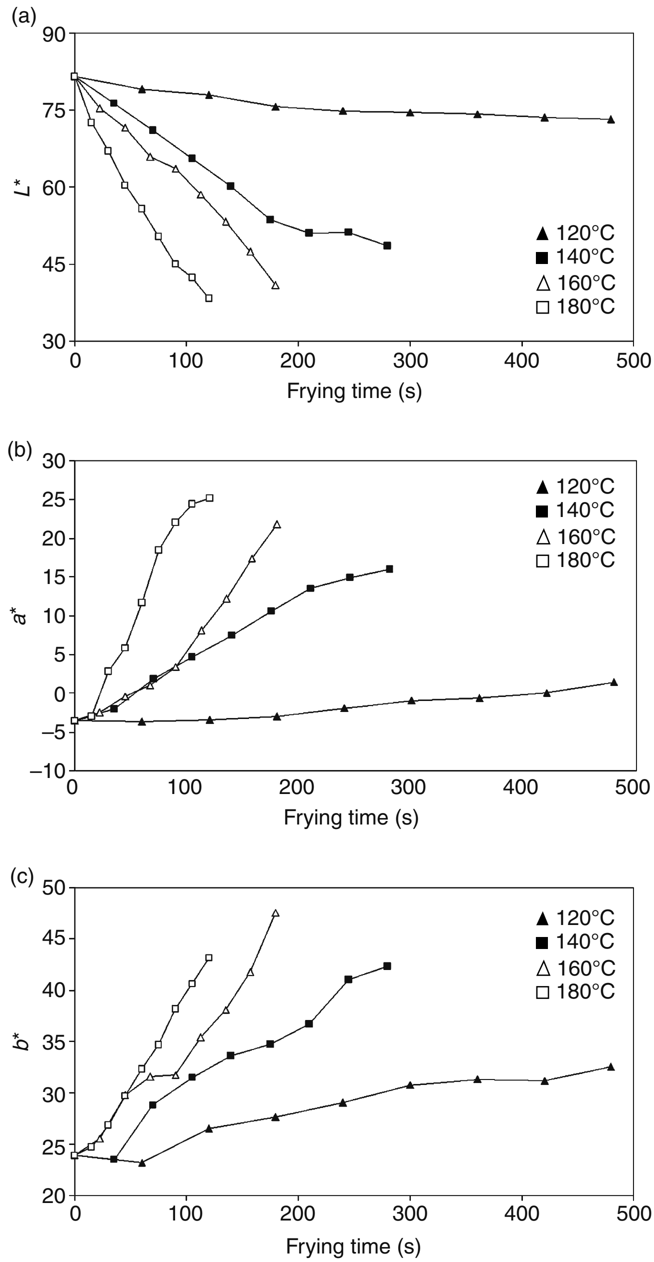



**FIGURE 5.6** Effect of frying temperature on color parameters of potato slices. (a) lightness, *L**; (b) redness, *a**; (c) yellowness, *b**.

blanched potato chips at the different temperatures tested (Pedreschi et al. 2007c) (Figure 5.8). In agreement with our results, it has been found that soaking potato slices in NaCl solutions of different concentration before frying originate paler potato chips (Santis et al. 2007). Potato slices tended to get darker after frying as the blanching temperature increased from 65 to 80°C (Santis et al. 2007).

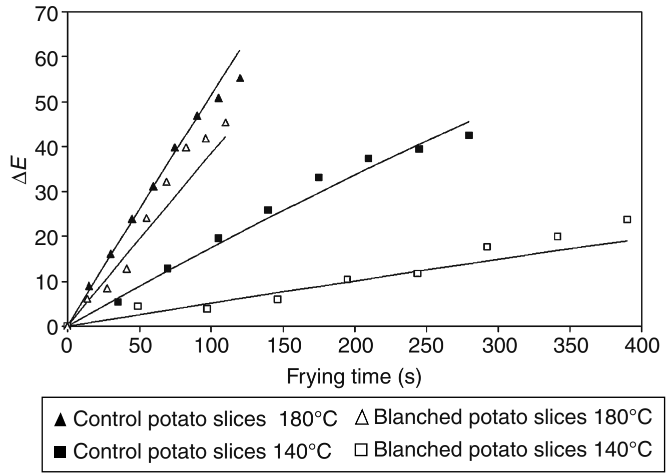



**FIGURE 5.7** Kinetics of total color changes ($\Delta E$) in potato slices. Experimental data and predicted by model Equation 5.4.

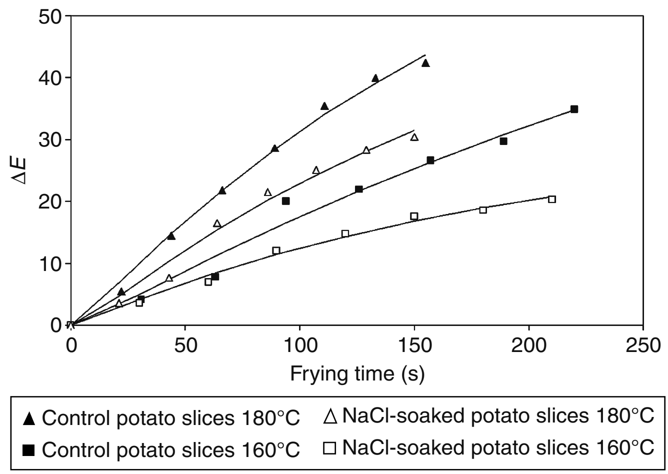



**FIGURE 5.8** Kinetics of total color changes ($\Delta E$) in potato slices. Experimental data and predicted by model Equation 5.4.

Air dehydration of potatoes prior to frying leads to a lower initial moisture content, typically 60% w.b. This reduction in moisture content reduces oil absorption of the final product (Gupta, Shivhare, and Bawa 2000; Krokida et al. 2001b; Moyano and Pedreschi 2006; Pedreschi and Moyano 2005a), but only a few researchers have studied the effect of pre-drying on the color of fried potatoes. A negative effect on color development with drying time was found by Krokida et al. (2001b). Pre-drying of potato slices led to paler potato slices than those of the raw potato slices after frying at 160 and 180°C (Figure 5.9). However, the differences in color ($\Delta E$) between the frying of blanched and pre-dried potato chips were not significant ($P > 0.05$) (Pedreschi et al. 2007a).

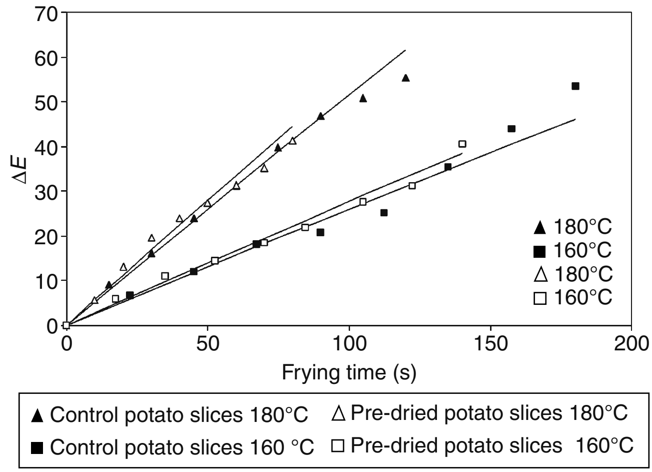



**FIGURE 5.9** Kinetics of total color changes ($\Delta E$) in potato slices. Experimental data and predicted by model Equation 5.4.

## 5.4 OIL UPTAKE

In fried potato cylinders, three oil fractions can be identified as a consequence of the different absorption mechanisms (Bouchon, Aguilera, and Pyle 2003): (i) structural oil, which represents the oil absorbed during frying; (ii) penetrated surface oil, which represents the oil suctioned into the food during cooling after removal from the fryer; and (iii) surface oil, which is the oil that remains on the surface. Bouchon, Aguilera, and Pyle (2003) showed that a small amount of oil penetrates during frying because most of the oil was picked up at the end of the process, suggesting that oil uptake and water removal are not synchronous phenomena.

Factors that affect heat and mass transfer during frying are the thermal and physical–chemical properties of the food and oil, the food geometry and the oil temperature. Most of the oil in the fried piece surface does not penetrate during frying; it adheres to the piece surface at the end of the frying and a high proportion of it penetrates into the food microstructure after frying (Aguilera and Gloria-Hernández 2000; Bouchon, Aguilera, and Pyle 2003; Ufheil and Escher 1996). Bouchon (2002) and Yamsaengsung and Moreira (2002) wrote an excellent review about different mathematical models developed to describe transport phenomena in fried foods. Only some researchers have considered the crust formation as a moving boundary problem in the modeling of the frying transport phenomena (Bouchon 2002; Farkas, Singh, and Rumsey 1996a, 1996b). On the other hand, few researchers have considered post-frying oil uptake in the models of mass transfer (Bouchon 2002; Durán et al. 2007; Yamsaengsung and Moreira 2002).

Some of the principal factors that affect oil absorption in fried products are: deterioration degree of the frying oil, temperature, pressure and frying time, food geometry, chemical composition of the raw food, pretreatments, surface roughness, and porosity of the food to be fried (Bouchon 2002; Saguy and Dana 2003). In general, oil uptake decreases at higher frying temperatures (Moreno and Bouchon 2008; Moyano and Pedreschi 2006; Moyano, Rioseco, and Gonzaléz 2002). Vacuum frying

allows reduction of oil content in fried potato and apple pieces (Garayo and Moreira 2002; Granda, Moreira, and Tichy 2004; Mariscal and Bouchon 2008; Moreno and Bouchon 2008). Usage of microwave in frying of potatoes (Oztop, Sahin and Sumnu 2007) and battered and breaded chicken (Barutcu, Sahin, and Sumnu 2007) has been studied recently. Although oil uptake was lower in microwave fried potatoes, higher oil contents were observed in microwave fried chicken fingers in comparison with traditional deep-fat frying.

Some treatments prior to frying allow significant reduction of oil uptake in fried products. Decreasing the initial moisture content of potatoes by air drying reduced the oil uptake (Pedreschi and Moyano 2005a). Potato strip impregnation in a 3% NaCl solution for 15 min produced French fries with lower oil content, which were crispier, and had a paler color (Bunger, Moyano, and Ríoseco 2003). On the other hand, application of edible films based on cellulose derivatives on the surface of potato strips has shown to reduce oil uptake (Khalil 1999; Mellema 2003; Rimac-Brncic et al. 2004). Several pre-frying treatments intend to reduce the absorption by reducing surface permeability. This can be achieved through edible film coating or direct blend modification (as in formulated products) using hydrocolloids such as methylcellulose, hydroxypropyl methylcellulose, long fiber cellulose, corn zein, starch and modified starch (Mellema 2003; Bouchon and Pyle 2004). Edible films and coatings could act as barrier not only to water loss during frying, but also for oil absorption when the food piece is removed from the fryer. Additionally, different batter and breading formulations can be used in fried foodstuffs such as chicken fingers, fish fingers, and chicken nuggets to improve the final sensorial attributes of the products and to modify the amount of fat absorbed by deep fat fried foods. They can also contribute to form a crispy and uniform layer in foods, providing enhanced visual and structural qualities, as well being tender and moist inside.

Although several works have found that most of the oil uptake occurs in the post-frying period (Bouchon, Aguilera, and Pyle 2003; Southern et al. 2000; Sun and Moreira 1994; Ufheil and Escher 1996), different approaches have been used to describe the kinetics of oil uptake during frying. Gamble, Rice, and Selman (1987) correlated oil content of potato slices with frying time and with square root of frying time. Kozempel, Tomasula, and Craig (1991) tried zero-order kinetics for French fries. Chen and Moreira (1997) applied energy and mass balance equations, solving the set of differential equations by means of the finite difference techniques, to model the oil content in tortilla chips. Krokida et al. (2001b) used first-order kinetics to describe the oil uptake in potato strips.

Moyano and Pedreschi (2006) studied the kinetics of oil uptake during frying at three temperatures of pretreated potato slices by applying two empirical kinetic models. In the first model, a mass balance for oil content during frying can be stated as:

$$O = O_{eq} - O^* \tag{5.9}$$

where $O$ is the oil content at time $t$ (in dry basis); $O_{eq}$ is the oil content at equilibrium (or maximum oil content) (in dry basis) at $t = \infty$ and $O^*$ is the oil content to be taken up between $t$ and $t = \infty$. It is assumed that $O^*/O$ is inversely proportional to frying time $t$, that is,

$$\frac{O^*}{O} = (Kt)^{-1} \tag{5.10}$$

Substituting in Equation 5.9, we have the model proposed by Moyano and Pedreschi (2006):

$$O = \frac{O_{eq}Kt}{1 + Kt} \tag{5.11}$$

$K$ represents the specific rate constant of oil uptake for this model. For short times, this model has a linear behavior with time, whereas for long times it becomes time-independent.

The second model is a first-order kinetics model (Krokida et al. 2001b):

$$O = O_{eq}^1\left(1 - \exp\left(-K^1t\right)\right) \tag{5.12}$$

Where $O^1_{eq}$ is the equilibrium oil content and $K^1$ is the specific rate constant for the first-order model. In both models at $t = 0$, oil content is null, and for long times, oil content reaches the equilibrium value.

For the frying of potato slices at temperatures of 120, 150 and 180°C, the fit of oil content versus time data to Equation 5.11 (proposed model) and Equation 5.12 (first-order kinetics) are shown in Figure 5.10 and Figure 5.11, respectively (Moyano and Pedreschi 2006). The fit of both models is similar, with a correlation coefficient, $r^2$ of 0.9786 for Equation 5.11 and of 0.9793 for Equation 5.12. For all the studied cases and for both models, the specific rate constants, $K$ and $K^1$ increased with frying temperature, whereas the equilibrium oil content values, $O_{eq}$ and $O^1_{eq}$ decreased with frying

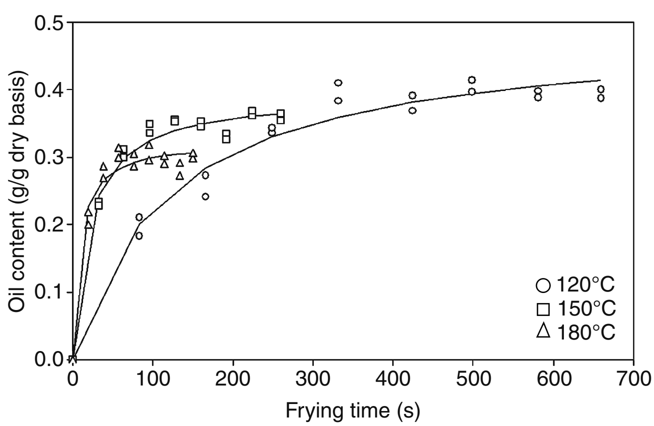



**FIGURE 5.10** Oil uptake for potato slices during frying. Experimental data and predicted by model Equation 5.11. (From Moyano, P. and Pedreschi, F., *Lebensmittel-Wissenschaft und- Technologie/Food Science and Technology (lwt),* 39. Kinetics of oil uptake during frying of potato slices: effect of pre-treatments, 281–291, copyright © 2006, with permission from from Elsevier).

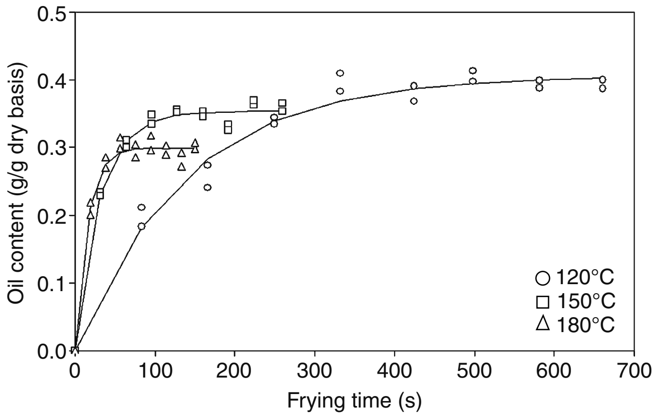



**FIGURE 5.11** Oil uptake for potato slices during frying. Experimental data and predicted by model Equation 5.12. (From Moyano, P. and Predreschi, F., *Lebensmittel-Wissenschaft und-Technologie/Food Science and Technology (lwt),* 39. Kinetics of oil uptake during frying of potato slices: effect of pre-treatments, 281–291, copyright © 2006, with permission from from Elsevier).

temperature. This behavior agrees with the hypothesis that higher frying temperatures lead to lower absorbed oil (Bouchon 2002; Moyano and Pedreschi 2006). Oil content was high even for short frying times at the three frying temperatures, suggesting that surface wetting is a crucial mechanism for oil absorption (Aguilera and Gloria-Hernández 2000; Bouchon, Aguilera, and Pyle 2003; Ufheil and Escher 1996).

Oil content versus moisture content in dry basis for potato slices fried at 120, 150 and 180°C is shown in Figure 5.12. There is a clear effect of the frying temperature on oil uptake at moisture contents $\leq$1 g water/g dry solid; the higher the frying temperature, the lower the oil content, with average values of 0.39, 0.35 and 0.30 g/g dry basis for 120, 150 and 180°C, respectively.

Durán et al. (2007) implemented a methodology to study oil partition that allowed accurate, easy and rapid determination of the structural oil content and the surface oil content fractions in potato chips. This method was corroborated because the sum of structural oil content and surface oil content was almost identical with the total oil content value determined experimentally by the methodology of (Bligh and Dyer 1959). Oil absorbed by blanched NaCl-impregnated potato chips was quantified during frying at 180°C (the post-frying stage is shown in Figure 5.13). During the initial period of frying ($\sim$40 s and later), the total oil content of the product increased considerably and then remained almost constant, even during the cooling stage. Final total oil contents in the product and its corresponding partition pattern relied on the frying temperature and pre-processing conditions. During frying at 180°C, only 38% of the total oil content of blanched NaCl-impregnated potato chips penetrated into their microstructure (structural oil content) and almost 62% remained in the product surface (surface oil content). Nevertheless, once the product was removed from the fryer (start of cooling stage), oil partition was inverted and about 65% of total oil content was absorbed while the rest remained on its surface. These results are in agreement with those of Ufheil and Escher (1996), who reported

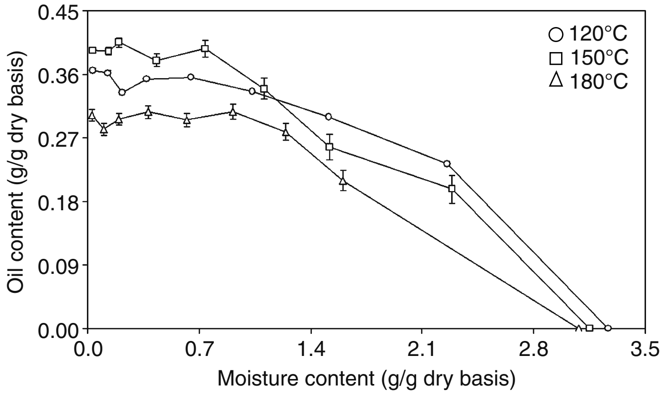



**FIGURE 5.12** Oil uptake *versus* moisture content during frying of potato slices. Lines connect experimental data corresponding to the same frying temperature. (From Moyano, P. and Pedreschi, F., *Lebensmittel-Wissenschaft und-Technologie/Food Science and Technology (lwt)*, 39. Kinetics of oil uptake during frying of potato slices: effect of pre-treatments, 281–291, copyright © 2006, with permission from Elsevier).

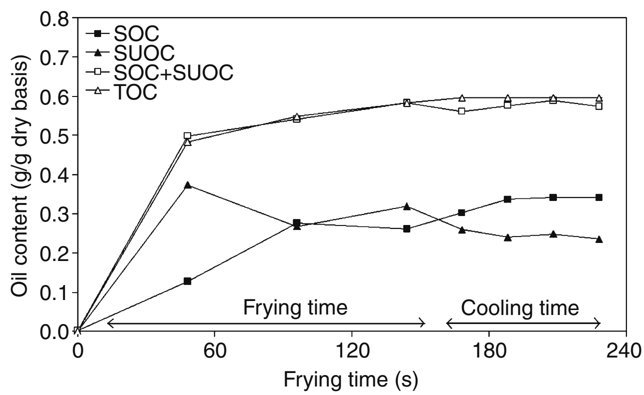



**FIGURE 5.13** Oil content distribution, structural oil content (SOC), surface oil content (SUOC) and total oil content (TOC) in blanched NaCl-impregnated potato chips during frying and cooling at 180°C. (From Durán, M., Pedreschi, F., Moyano, P., and Troncoso, E., *Journal of Food Engineering,* 81. Oil partition in pre-treated potato slices during frying and cooling, 257–265, copyright © 2007, with permission from Elsevier).

that most of the oil during frying of potato chips was absorbed when the slices were removed from the fryer.

## 5.5 TEXTURE

Texture is a sensory perception, which means that only humans can perceive, describe and quantify it. It is generally described as a multi-parameter attribute, usually associated with mechanical, geometrical and acoustic parameters (Szczesniak 1987). The accepted definition of texture was proposed by Szczesniak (1963), whereby "texture

is the sensory and functional manifestation of the structural and mechanical properties of foods, determined by the senses of vision, hearing, touching and kinesthetic". Texture is defined by the structural properties of food (Aguilera and Stanley 1990). Interactions between perceived texture and physical structure are complex, particularly for fruits and vegetables.

Textural changes during frying are the result of many physical, chemical and structural changes produced in raw tissues which also include heat and mass transfer with chemical reactions. In products with relatively high starch content such as potatoes, the major influence on texture could be gelatinization of starch during heating (Andersson et al. 1994). Frying of raw vegetables induces major changes in its microstructure that in turn determine their final physical and sensory properties. It is therefore important to characterize the changes in the texture of vegetable tissue during frying. Texture is also an important physical property in battered and breaded food products. Frying battered/breaded products forms a crisp, continuous and uniform layer over the food substrate, which constitutes its final outer coating. Crispy coatings are a critical part of the popularity of fried food (Mellema 2003).

Studies on the fundamental mechanical properties in fried potatoes are useful to quantify changes in structural parameters such as crispness and hardness, which are of primary importance for fried potato processing companies (Ross and Scanlon 2004). Several procedures (subjective and objective) have been used to quantify the texture of some foodstuffs (e.g., fried potatoes) (Du Pont, Kirby, and Smith 1992; Katz and Labuza 1981; Kulkarni, Goviden, and Kulkarni 1994; McComber, Lohnes, and Osman 1987; Verlinden, Nicolaï, and J. De Baerdermaeker 1995). Bourne, Moyer, and Hand (1966) carried out a puncture test on potato chips and measured the initial slope from the force–deformation curve. The maximum force of break varied considerably, and the initial slope was more reproducible. They recommended this parameter to measure crispness. Solids distribution, oil spots/pockets, and crust frying patterns (e.g., whether potato samples are cooked over a layer of hot oil, are partially or fully submerged) contribute to the variability in texture of the fried potatoes. In spite of its variability, the puncture test gives excellent discrimination between the mechanical properties of the crust, and can be used for products of different sizes and shapes because it is less sensitive to the cross-sectional geometry of the product (Texture Technologies Corporation 1995). Segnini, Dejmek, and Öste (1999b) developed a puncture test with three support points to evaluate the texture of potato chips. This procedure gave less variation in analytic results and permitted the correlation of texture with moisture content. Pedreschi, Aguilera, and Pyle (2001) also developed a puncture test to measure *in situ* textural changes in potato strips during frying. This test allowed testing potato strips at different positions and at different frying times inside the hot oil, avoiding the cooling process that takes place when the strips were removed from the fryer and which could affect their mechanical properties.

Figure 5.14a shows a puncture test for potato chips where the sample was mounted over a three-point support where the distance between points was 15 mm, and the punch diameter was 5.3 mm (Pedreschi, Segnini, and Dejmek 2004). Maximum force of break (MFB; force required to break the structure of the chip) and the deformation of break (DB; distance corresponding to MFB) were extracted from the force–distance curve obtained (Figure 5.14b). On the other hand, for

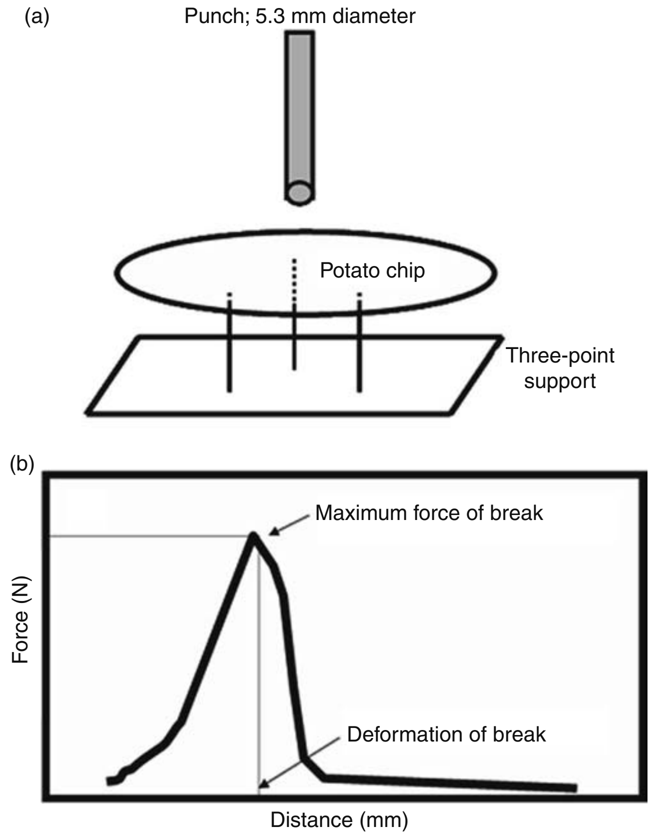



**FIGURE 5.14** Texture measurement of fried potato slices. (a) Slice puncture test; (b) Typical force–distance curve from the Instron Universal Testing Machine. (From Pedreschi, F., Segnini, S., and Dejmek, P., *Journal of Texture Studies,* 35. Evaluation of the texture of fried potatoes, 277–291, copyright © 2004, with permission from Food & Nutrition Press, Incorportaed).

the puncture test for French fries, potato strips were mounted over a two-point support, where the distance between points was 30 mm, and the punch diameter was 5.3 mm (Figure 5.15a). Maximum force of deformation (MFD; force required to break the strip after an initial bending and the maximum deformation (MD) defined as the distance corresponding to MFD were extracted from the force–distance curve obtained (Figure 5.15b).

Texture degradation of vegetable tissues during frying shows an initial softening followed by hardening of the tissue. A model with the sum of two terms has been proposed: the first for softening with first-order kinetics and the second one for hardening which, in the case of potato chips, is dependent on the square of time (Pedreschi and Moyano 2005b) and, in the case of French fries, is linearly dependent on time (Pedreschi, Aguilera, and Pyle 2001). Higher frying temperatures accelerated cooking of the core and hardening of the crust, resulting in French fries with harder crusts. For potato chips, frying showed an initial stage in which the potato tissue

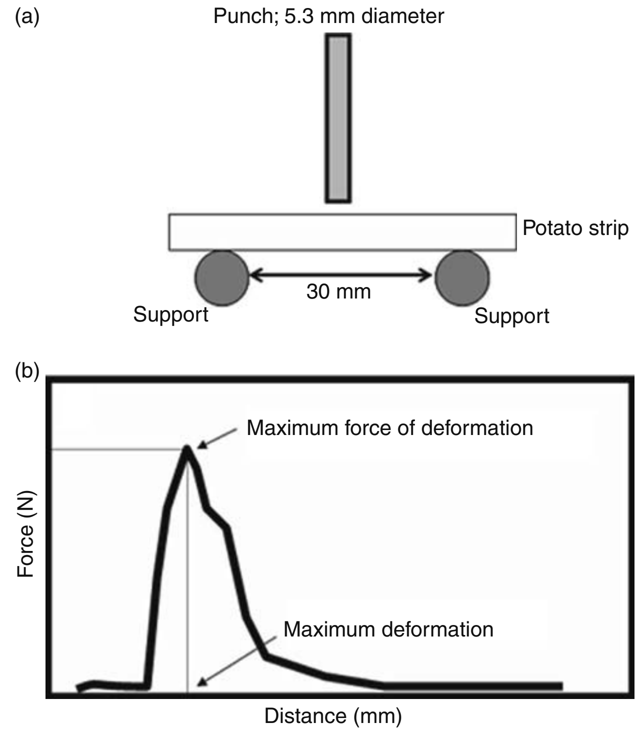



**FIGURE 5.15** Texture measurement of fried potato strips. (a) Strip bending test; (b) Typical force–distance curve from the Instron Universal Testing Machine. (From Pedreschi, F., Segnini, S., and Dejmek, P., *Journal of Texture Studies,* 35. Evaluation of the texture of fried potatoes, 277–291, copyright © 2004, with permission from Food & Nutrition Press, Incorportaed).

softened and became cooked, and a later stage in which the crust formation started and progressively hardened (Pedreschi and Moyano 2005b). Processing conditions strongly affect the textural properties of potato chips and French fries (Agblor and Scanlon 1998; Pedreschi and Moyano 2005a, 2005b, Pedreschi, Segnini, and Dejmek 2004).

Pedreschi and Moyano (2005b) modeled textural changes in potato slices during frying using the parameter normalized maximum force, $MF^*$ (value of $MF$ at any time divided by the value of $MF$ at time zero). $MF^*$ allowed softening of the tissue and crust development processes to be followed during frying because it represents the force required to penetrate the sample. The following Equation was used to describe the variation of $MF^*$ with frying time:

$$MF^* = \exp\left(-k_s t\right) + k_h t^2 \tag{5.13}$$

where $MF^*$ = normalized maximum force; $k_s$ = kinetic constant for softening of the potato tissue during frying ($s^{-1}$); $k_h$ = kinetic constant for the crust hardening process during frying ($s^{-2}$) and $t$ = frying time (s).

The first term in Equation 5.13 represents an initial decrease in *MF** due to the softening of the potato tissue for short frying times originated by lamella media solubilization and starch gelatinization (Andersson et al. 1994). The second term represents the development of the crust (hardening) at longer frying times. The overall texture of a potato chip at any frying time is characterized by these two terms. The kinetics of textural changes in potato slices during frying at 120, 150 and 180°C was studied using the normalized textural parameter *MF** (Figure 5.16). Initial softening of potato tissue ($t < 166$ s) and development or hardening of the crust ($t > 166$ s) during frying at 120°C can be followed simultaneously using Equation 5.13 (Figure 5.16). A similar trend was found in potato slices fried at 150 and 180°C.

Pedreschi and Moyano (2005a) determined that maximum force for fried potato slices after blanching and blanching plus drying increased as the moisture content of the pieces decreased below 50 g/100 g, indicating an increase in the crispness of the chips (Figure 5.17). Pre-drying induced a reduction of ~15 and ~17% in the initial maximum force and moisture content of the blanched slices, respectively. Blanched and dried chips have higher maximum force than only blanched potato chips, i.e., blanched and dried potato chips were much crispier than only blanched potato chips. For moisture contents < 10 g/100 g, the frying temperature was effective on maximum force when slices with the same moisture contents were compared. Potato chips fried at 120°C were significantly crispier than potato chips fried at 180°C, although they have approximately the same moisture contents (~1.8 g/100 g (w.b.)). Pre-drying had a significant effect ($P < 0.05$) on increasing the final texture (represented by maximum force) of the final blanched fried potato slices.

Moyano, Troncoso, and Pedreschi (2007) recently proposed a kinetic model based on irreversible chemical reactions in series to fit experimental data of texture

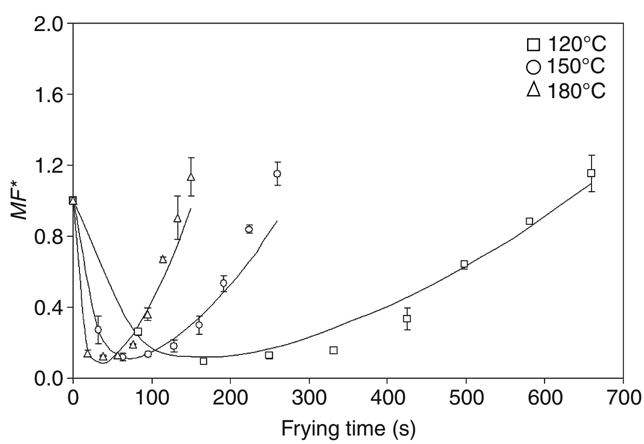



**FIGURE 5.16** Kinetics of softening and hardening of the control potato slices during frying represented by the normalized textural parameter maximum force (*MF**). Experimental data and predicted by model Equation 5.13. (From Pedreschi, F. and Moyano, P., *Journal of Food Engineering*, 70. Oil uptake and texture development in fried potato slices, 557–563, copyright © 2005, with permission from Elsevier).

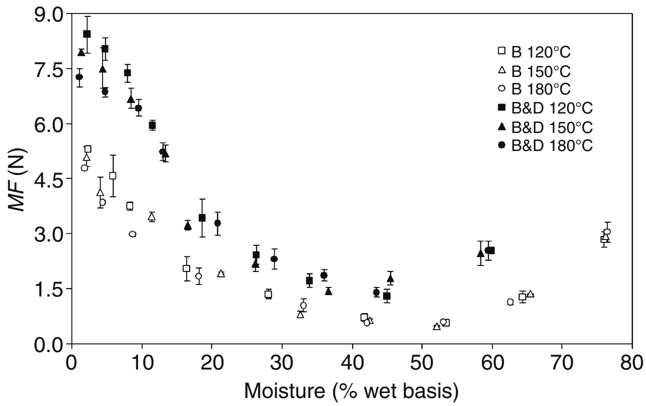



**FIGURE 5.17** Maximum force *versus* moisture content for potato slices fried at 120, 150 and 180°C. B: blanched; B&D: blanched and dried. (From Pedreschi, F. and Moyano, P., *Lebensmittel-Wissenschaft und-Technologie/Food Science and Technology (lwt),* 38. Effect of pre-drying on texture and oil uptake of potato chips, 599–604, copyright © 2005, with permission from Elsevier).

changes during thermal processing of potato products. The model links dimensionless maximum force $F^*_{\mathrm{MAX}}$ with processing time. During thermal processing, the raw tissue becomes progressively softer and, in the case of severe treatment, it later turns hard. The proposed model considers these changes as irreversible chemical reactions in series, which can be stated as:

$$R(raw\ tissue) \xrightarrow{k_1} S(soft\ tissue) \xrightarrow{k_2} H(hard\ tissue) \tag{5.14}$$

It was assumed that the concentration of these three kinds of tissues will change during processing with first-order kinetics. For raw tissue:

$$-\frac{dC_{\mathrm{R}}}{dt} = k_1 C_{\mathrm{R}} \tag{5.15}$$

For soft tissue:

$$\frac{dC_{\mathrm{S}}}{dt} = k_1 C_{\mathrm{R}} - k_2 C_{\mathrm{S}} \tag{5.16}$$

and for hard tissue:

$$\frac{dC_H}{dt} = k_2 C_S \tag{5.17}$$

Assuming that at the beginning of the process ($t=0$) there is only raw tissue ($C_{\mathrm{R0}}$), this means that $C_{\mathrm{S0}} = C_{\mathrm{H0}} = 0$, the solution of Equation 5.15, Equation 5.16 and Equation 5.17 gives:

$$\frac{C_\mathrm{R}}{C_\mathrm{R,0}} = e^{-k_1 t} \tag{5.18}$$

$$\frac{C_\mathrm{S}}{C_\mathrm{R,0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{5.19}$$

$$\frac{C_\mathrm{H}}{C_\mathrm{R,0}} = 1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} - e^{-k_2 t} \tag{5.20}$$

In Equation 5.19, $k_1$ represents the specific disappearance rate of the raw tissue, whereas $k_2$ is the specific disappearance rate of the soft tissue. The disappearance of soft tissue implies the appearance of hard tissue. In this way, Equation 5.19 contains the net rate of change for soft tissue allowing the calculation of its dimensionless concentration.

At $t = 0$ the maximum force is proportional to the concentration of raw tissue:

$$F_\mathrm{MAX,0} = K' C_\mathrm{R,0} \tag{5.21}$$

and the model proposes that for times, $t > 0$:

$$F_\mathrm{MAX} = F_\mathrm{MAX,0} K'' C_\mathrm{S} \tag{5.22}$$

It follows that a dimensionless maximum force $F^*_\mathrm{MAX}$ can be expressed as:

$$F^*_\mathrm{MAX} = \frac{F_\mathrm{MAX}}{F_\mathrm{MAX,0}} = 1 - K\frac{C_\mathrm{S}}{C_\mathrm{R,0}} \tag{5.23}$$

where $K$ is the proportionality constant linking texture with dimensionless concentration of soft tissue. Substituting Equation 5.19 into Equation 5.23, the main equation of the model is obtained:

$$F^*_\mathrm{MAX} = 1 - \frac{Kk_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{5.24}$$

The kinetics of textural changes in French fries during frying at 160, 170 and 180°C was studied using the dimensionless maximum force $F^*_\mathrm{MAX}$ (Figure 5.18). Initial softening of potato tissue ($t \leq 80$ s) and development of the crust ($t \geq 80$s) during frying can be followed simultaneously using Equation 5.24. The specific rate $k_1$ represents an initial decrease in $F^*_\mathrm{MAX}$ linked to the softening of the potato tissue for the first period of frying originated by lamella media solubilization and starch gelatinization (Andersson et al. 1994). The specific rate $k_2$ represents the development of the crust at longer frying time, whereas $K$ is a proportional constant linking texture with dimensionless concentration of soft tissue (Moyano, Troncoso, and Pedreschi 2007).

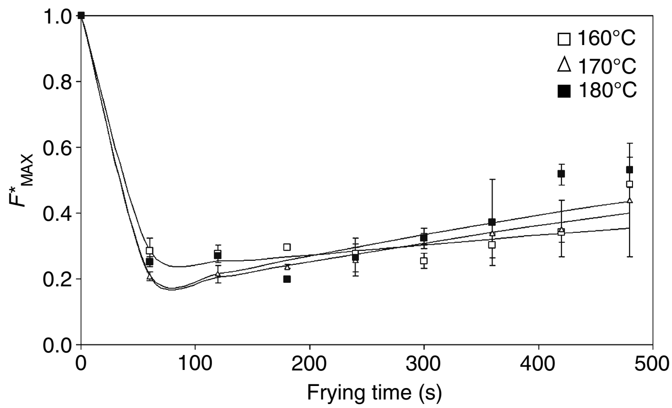



**FIGURE 5.18** Kinetics of texture change during frying of French fries represented by the dimensionless maximum force $F^*_{MAX}$. Experimental data and predicted by model Equation 5.24. (From Moyano, P., Troncoso, E., and Pedreschi, F., *Journal of Food Science,* 72. Modeling texture kinetics during thermal processing of potato products, 102–107, copyright © 2007, with permission from Institute of Food Technologists).

## 5.6 VOLUME AND POROSITY

Porosity and volume are important physical properties in raw and fried vegetables because they are strongly linked to their mechanical properties and microstructure. The violent formation of bubbles generated in potato tissue during frying originates an structure with variable porosity in time and which is affected by the operational parameters (Moreira, Castell-Perez, and Barrufet 1999). Shrinkage (volume decreasing) and deformation depend on food geometry, drying method and drying conditions.

Porosity ($\phi$) is very important in fried products and is defined as:

$$\phi = 1 - \frac{\rho_b}{\rho_s} = 1 - \frac{V_s}{V_b} \tag{5.25}$$

where $\rho_s$ is the solid density, defined as the material mass divided by the real solid material volume (including water) excluding the pore volume. The solid volume without pore volume could be measured using a stereopycnometer (Karanthanos and Saravacos 1993). $\rho_b$ is the total density and defined as the material mass divided by the total material volume. The total volume of irregular forms (such as those produced during frying of potatoes and tortillas) could be measured by volumetric displacement using 100-μm diameter glass beads (Marousis and Saravacos 1990; Moreira, Castell-Perez, and Barrufet 1999; Pinthus, Weinberg, and Saguy 1995).

Density and porosity of fried products change dramatically due to shrinkage, and affect the vegetable transport properties such as thermal and mass diffusivity (Krokida and Maroulis 1999). Roughness is an important physical property which affects processes strongly related to food surface. An appropriate example is oil

uptake in fried products, which is entirely a surface phenomenon (Bouchon 2002; Moreira, Sun, and Chen 1997; Pedreschi, Aguilera, and Arbildua 1999). Some authors have used fractal geometry to calculate roughness in fried potatoes, while others have used statistical methods (Bouchon and Pyle 2004; Pedreschi, Aguilera, and Brown 2000; Rubnov and Saguy 1997).

Pinthus, Weinberg, and Saguy (1992) determined that the crust porosity of fried restructured potato product decreased throughout frying, and was markedly affected by lower gel strengths. Pinthus, Weinberg, and Saguy (1995) determined that the porosity of a restructured potato product ranged from 0.089 to 0.168 after fluctuating subfreezing storage temperatures. A linear relationship was found between oil uptake during frying and porosity prior to frying. Particle density increased, bulk density decreased, and porosity increased noticeably during frying. After an initial short period, oil uptake was correlated linearly with porosity of the fried product. A new term, "net porosity" which excluded the void volume occupied by oil was developed for describing the mechanism of oil uptake. Krokida, Oreopolou, and Maroulis (2000) studied the effect of frying conditions on shrinkage and porosity of fried potatoes. Apparent density, true density, specific volume and internal porosity were investigated during frying and had a strong effect on moisture loss and oil uptake during frying. Porosity of French fries increases with oil temperature and sample thickness, and is higher for products fried with hydrogenated oil. On the other hand, Moreira, Sun, and Chen (1997) determined that tortilla chips prepared from finely ground masa showed excessive puffing, resulting in higher oil absorption and lower porosity, whereas tortilla chips made from coarse particles presented the lowest oil content and no puffing. Figure 5.19 shows the effect of frying time and temperature on the porosity changes in potato slices during frying. At longer times and higher frying temperatures, the porosity increased considerably. Experimental data was fitted to Equation 5.26.

$$\phi = a(b - \exp(-ct)) \tag{5.26}$$

where *a, b* and *c* are the parameters of the model and *t* is the frying time.

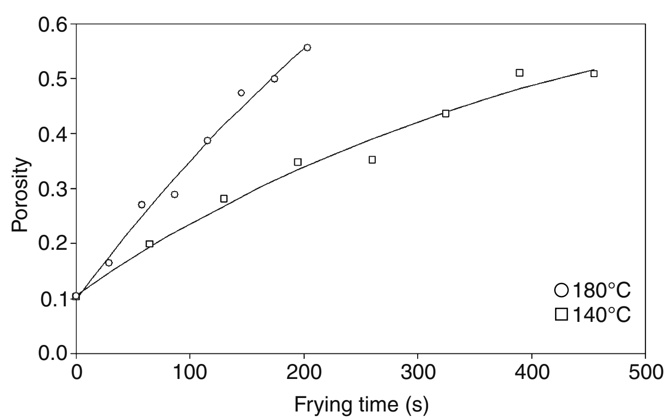



**FIGURE 5.19** Kinetics of porosity change for potato slices during frying. Experimental data and predicted by model Equation 5.26.

## 5.7 ACRYLAMIDE CONTENT

The neurotoxic and carcinogenic compound acrylamide is found in heat-processed food such as fried products prepared with high starch raw materials. It is mainly formed from asparagine and a reducing sugar through Maillard reactions, which also generate compounds responsible for the brown color and important flavor components of heated food (Mottram and Wedzicha 2002; Stadler et al. 2002; Zyzak et al. 2003). The initial concentration of the precursors, their ratio, heating temperature, time of processing, pH and water activity of the product, have been found to influence the acrylamide content in heat-processed foods (Yaylayan, Wnorowski, and Pérez Locas 2003).

Acrylamide concentrations found in fried products are the result of simultaneous formation and elimination (Biedermann et al. 2002). The mechanism(s) of acrylamide elimination, however, remains unknown. Formation and elimination of acrylamide is known to be affected by frying temperature, type and concentration of sugars, surrounding food matrix, pH, water content, and the concentration of asparagine. Because the amount of free asparagine in potato tubers greatly exceeds the amount of reducing sugars, the latter determines the degree of acrylamide formation and Maillard browning upon frying (Amrein et al. 2003). In practice, reducing sugar contents $< 1$g/kg fresh weight are an indicator of suitable product quality. To obtain this goal, several techniques such as hot-water blanching and soaking have been applied prior to frying to partially extract accumulated sugars from the raw material (Pedreschi et al. 2004; Pedreschi, Kaack, and Granby 2006) but these adjustments also affect the color of the fried product (Krokida et al. 2001b; Pedreschi et al. 2005a). In addition, the higher the frying temperature, the higher the acrylamide formation in fried potatoes and the darker the color generated in potato chips and French fries. Vacuum frying allows reducing acrylamide content in potato chips (Garayo and Moreira 2002; Granda, Moreira, and Tichy 2004).

Color measurement may be used as an easy, assessable and fast indicator of acrylamide content because Maillard reaction browning and acrylamide formation are to some extent related. Recently, several researchers investigated the relation between the content of acrylamide and surface color in fried potatoes (Pedreschi et al. 2005a; Pedreschi, Kaack, and Granby 2006; Pedreschi et al. 2007c). However, it was observed that this correlation was not so good for large surface-to-volume material (e.g., potato chips) in comparison with small surface-to-volume material (e.g., French fries). In addition, very extensive frying caused dark colored foodstuffs, but lower acrylamide contents due to degradation phenomena (Granda, Moreira, and Tichy 2004). However, while glucose and asparagine increased acrylamide formation, only glucose caused a significantly different product in the color of the final fried product (Granda, Moreira, and Tichy 2004).

Granda (2005) determined the kinetics of acrylamide formation during traditional and vacuum frying at different temperatures. Acrylamide accumulation under vacuum fry ing was modeled using first-order kinetics, and during traditional frying it was modeled using the logistic model. The behavior of the kinetics of acrylamide content in potato chips fried under the two processes was different mainly due to the different frying temperatures used. During traditional frying, higher temperatures were used (150°C and 180°C) and acrylamide was produced after some time, but it also started degrading, producing a constant level of acrylamide at longer times.

During vacuum frying (10 Torr, 120°C), acrylamide increased exponentially (but at lower levels) for all frying times.

## 5.8 CONCLUSIONS

Frying temperature has a strong effect on mass transfer during frying processes. Water loss and effective moisture diffusivity increases with frying temperature. Frying temperature has a significant effect on the final oil content of fried potato slices. The higher the frying temperature, the lower the oil uptake in the fried potato slices.

Color is affected by frying temperature and time. The resultant fried products get darker as a result of non-enzymatic browning reactions that are highly dependent on oil temperature and frying time. In potato products, pretreatments improve the color of potato chips and French fries.

CV allows determination of the color of fried potatoes in an easy, precise, representative, objective and inexpensive way. Also, it allows measurements of the color over the entire surface of a product or over a small specific surface region of interest.

The dynamic method is more advantageous for the studies on color kinetics. It is used to calculate the activation energies of the reactions as a function of potato moisture content instead of getting a unique mean value for *Ea,* giving a more realistic picture of non-enzymatic browning extent during frying.

Texture development in a fried potato piece shows two stages: (i) a stage in which the tissue softens; (ii) a stage in which an external crust begins to form and hardens progressively with time as the moisture content diminishes. Higher frying temperatures accelerate these stages. A kinetic model based on irreversible chemical reactions in series has been proposed to fit experimental data of texture changes during thermal processing of potato products. This model links dimensionless maximum force $F^*_{MAX}$ with processing time.

The porosity of potato slices increases with frying time and temperature, and relies strongly on the pre-processing conditions on the potato tissue.

Frying temperature has a strong effect on the kinetic of acrylamide formation; the higher the temperature, the higher the acrylamide formed. In most cases, the mechanism of acrylamide formation seems to be strongly linked to the Maillard reaction.

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# 6 Physical Properties of Fried Products

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**CONTENTS**



## 6.1 INTRODUCTION

Deep-fat frying is a process of cooking foods by immersing them in edible fat or oil at a temperature above the boiling point of water, usually 150–200°C for a specific period of time. It is very popular and one of the oldest methods of food preparation for more than 3000 years (Stier 2004). Frying is popular throughout the world, not only in industrial food manufacturing, but also in restaurants and domestic food preparations. The production of high-quality food is the purpose of frying. The objective of deep-fat frying is to produce foods for immediate consumption or for additional processing. Many foods have been successfully deep-fat fried, such as potato chips, French fries, donuts, extruded snacks, fish sticks and fried chicken products. Deep-fat frying is a complicated cooking and drying process accomplished in hot oil in which heat and mass transfer take place simultaneously. Convective heat transfer takes place from the oil to the food surface, and then conductive heat transfer into the interior of the food. Also, mass transfer occurs due to oil uptake into the product, and the release of water in the form of vapor from the food through the oil (Miranda and Aguilera 2006).

Deep-fat fried food is popular due to its unique flavor and texture. A crust is developed on the food surface, providing most of the texture, color and flavor for which fried foods are known and desired. The core region provides the bulk of the mass, moisture, and nutrients in the fried foods, and contributes to the texture during consumption (Farinu and Baik 2005; Varela, Bender, and Morton 1988). This typically leads to dry and crispy crust, and tender inside. At the same time, typical frying flavor is provided by Maillard reactions in the crust (Mellema 2003). The quality of fried food is dependent on: appearance (color, shape, gloss), flavor (taste, odor), texture, and nutrition (Bourne 1982). The quality characteristics of fried foods can be determined by measuring the related product properties. For example, consumers of potato chips like a tasty product with a crispy golden crust. In this chapter, the variations in physical properties of various foods during frying are reviewed. Selected physical properties of foods are: (i) geometric properties (shape, size, surface area, volume and density); (ii) thermal properties (thermal conductivity, thermal diffusivity, specific heat, heat transfer coefficient); (iii) mass transfer properties (moisture diffusivity, fat diffusivity, mass transfer coefficient); (iv) optical properties (color, surface appearance); and (v) mechanical properties (hardness, cohesiveness, viscosity, springiness, adhesiveness, textural properties).

Geometric properties include shape, size, surface area, specific volume, porosity and density. Foods generally change shape after frying. The shape of an object is described by roundness and angle of curvature. The visual color and surface appearance are two important optical properties. Color is one of the most important quality attributes having psychological connotations that can influence the emotional state and mood of consumers. The color of fried products is the first impression perceived by consumers. For example, most people may like golden yellow-fried chicken, whereas the dark brown variation is not so welcome (Rossell 2001). Color description by spectrophotometric methods is based on: reflectance (lightness), dominant wavelength (hue), and purity (chrome or intensity). The International Standard color parameters are L*, a* and b* (or Hunter color scale L, a and b). The L* defines the lightness, a* refers to the red-green hues, and b* refers to the blue-yellow hues (Peleg and Bagley 1983). The thermal properties of foods such as specific heat (Cp), thermal conductivity (k), heat transfer coefficient (h) and thermal diffusivity ($\alpha$) are important because they govern the change of food temperature during frying. The k of fried foods depends on their porosity, structure and chemical constituents, primarily based on the properties of air, fat and water. $\alpha$ is related to k, density ($\rho$), and Cp of the product ($\alpha = k/(\rho.\ Cp)$). It determines the rate of heat propagation through the food.

Crispness is an important texture characteristic of fried foods. Crispness indicates freshness and high quality (Szczesniak 1988). For example, a crisp fried food should be firm and should snap easily when deformed, emitting a crunchy sound (Christensen and Vickers 1981). Chapter 5 provides detailed information on the quality (including color and texture) kinetics of fried foods, this area is not discussed in detail in this chapter.

Factors affecting the physical properties of fried food are their moisture and oil contents, and process conditions (Moreira, Castell-Perez, and Barrufet 1999). During frying, the physical, chemical and sensorial characteristics of food are modified. The quality of fried potatoes depends mainly on their structural, textural and optical

properties. Most important structural properties such as apparent and true density, porosity and specific volume of fried foods change during frying. Oil temperature significantly affects all structural properties. Increase in oil temperature decreased true and apparent density of fried potatoes while porosity increased (Blumenthal and Stier 1991). Change in the physical properties of materials during frying also affects the rate at which heat and mass are transferred.

## 6.2 GEOMETRIC PROPERTIES

### 6.2.1 Shrinkage

Shrinkage is the change in dimensions and size of the product being fried. Potato thickness decreased exponentially with time during frying (Costa, Oliveira, and Boutcheva 1997). Shrinkage rate increased with frying temperature and decreased with potato thickness, yet the final volume was not affected by temperature. Volume decreased mainly as a result of water loss, except for very low water content, and thus potato density did not suffer major changes. At the end of frying (and particularly for small samples and high frying temperatures), volume increased because of oil uptake and accumulation of entrapped water vapor (Costa, Oliveira, and Boutcheva 1997). For French fries (Krokida, Oreopoulou, and Maroulis 2000a), oil uptake and water loss increased as oil temperature increased and sample thickness decreased. Shrinkage was negligible during frying. With the increase in oil temperature and decrease in sample thickness, specific volume decreased (Krokida, Oreopoulou, and Maroulis 2000b).

For sweet potato fried in canola oil at 170°C, shrinkage increased with frying time, reaching a maximum at 120 s, and decreased or leveled off afterward (Taiwo and Baik 2007). Shrinkage first occurred at the product surface and then moved inside with frying. Maximum change in sample diameter ranged between 6.7 and 10.2% depending on pretreatment. Maximum change in disc thickness observed at 120 s of frying was 18.3%.

A tofu disc shrank by 9.0–13.5% during frying at 147–172°C in liquid canola shortening (Baik and Mittal 2005). Frying at higher oil temperature resulted in greater shrinkage at the same frying period. This was due to higher moisture transfer rate of the tofu disc, with the higher product temperature resulting from frying at higher oil temperature. For all frying conditions, 50% of shrinkage occurred within about one-third of total frying time.

Tortilla chips are one of the most popular masa-based snack products. When tortilla chips were fried in fresh soybean oil at 190°C for 60 s, most of the shrinkage of tortilla chips occurred during the first 5 s of frying (Kawas and Moreira 2001). Chip thickness increased by about 40% because of crust formation, and some bubbles developed at the surface due to vapor generation. The crust thickness increased nonlinearly with decrease in moisture content during frying. Tortilla chips decreased in diameter by about 9%, expanded in thickness by 10%, and puffed by 100% at the end of frying. The chips became more porous (pore size increased in number and size) at the end of frying due to the decrease in bulk density caused by water loss. The distribution of pore size became more uniform, and the number of large pores

increased, filling out the entire structure of the chips in a normal distribution as frying time increased (Kawas and Moreira 2001). When shrinkage began to stop, puffing commenced (Yamsaengsung and Moreira 2002). Crust formation at the outer layer of the chip restricted the amount of pressure that could be released from the core region. Puffing began at about 10% moisture content in wet basis (w.b.) and continued until about 2%.

Maximum expansion of donut was observed at different processing times at different temperatures, e.g., 77.9% of expansion for 120 s at 180°C, 71.4% for 105 s at 190°C, and 37.3% for 75 s at 200°C (Velez-Ruiz and Sosa-Morales 2003a).

### 6.2.2 Density

Apparent or bulk density, true or solid or particle density, specific volume and internal porosity were investigated during potato frying in refined and hydrogenated cottonseed oil (Krokida, Oreopoulou, and Maroulis 2000a). Apparent density and specific volume decreased during frying, whereas true density and porosity increased. Oil temperature affected all structural properties significantly. For example, increase in oil temperature decreased true and apparent densities of fried potato, and increased total porosity. The opposite trends were observed for sample thickness. That is, as sample thickness increased, true and apparent densities and specific volume of fried potato increased, but total porosity decreased (Krokida, Oreopoulou, and Maroulis 2000a). For French fries (cross sections of $5 \times 5$, $10 \times 10$ and $15 \times 15$ mm$^2$, 40-mm length and 150, 170, 190°C oil temperature), true density was 1117 kg/m$^3$ (Krokida, Oreopoulou, and Maroulis 2000b). True density increased with moisture loss, but decreased with oil uptake. Increasing sample thickness increased true density because sample thickness increase resulted in a decrease in oil content and increase in water content for the same frying time. Oil type also affected the true density because hydrogenated oil has a higher density than refined oil. True density increased as concentration of hydrogenated oil increased. The apparent density decreased during frying due to water loss, oil gain and pore development. Increase in oil temperature decreased apparent density because mass transfer rate increased due to the increase in oil temperature. Apparent density also increased with increase in sample thickness, and was higher when frying in hydrogenated oil.

When sweet potato discs were pretreated and fried in canola oil at 170°C for 0.5–5 min, the bulk density of the fried samples decreased during frying (Taiwo and Baik 2007). The values of bulk density were 1180–1270 kg/m$^3$ initially and 760–940 kg/m$^3$ after 5 min of frying. The true density values were 1026–1160 kg/m$^3$ initially and 1190–1280 kg/m$^3$ at the end of frying, indicating a slight increase. The bulk density of potato decreases linearly with frying time because of the significant weight loss as a result of water evaporation, and is not accompanied by an identical decline in sample dimensions when fried in refined and hydrogenated groundnut oil (Rani and Chauhan 1995).

Velez-Ruiz and Sosa-Morales (2003a) studied the variation of apparent density of donuts during frying. Dough, based on wheat flour and yeast as leavening agent, was fried in sunflower oil at 180, 190, and 200°C to produce donuts. The bulk density of dough was 526.9 kg/m$^3$, changing immediately as the frying began, showing

a decreasing trend with extreme values of 465 kg/m$^3$ and 310 kg/m$^3$ as a function of frying time, oil temperature and ingredient characteristics. The bulk density of the pastry mix dough was 836 kg/m$^3$ when fried in canola liquid shortening at 150°C (Williams and Mittal 1999).

The bulk density values (219–366 kg/m$^3$) of chickpea flour suspension fried at 175°C in groundnut oil were significantly lower than those of fresh suspension (1114 kg/m$^3$). A sharp decrease in the bulk density values in the initial stage (within 20 s) of frying was due to expansion caused by sudden loss of moisture from the product (Bhat and Bhattacharya 2001).

The bulk density of tofu was 1053–1251 kg/m$^3$ for moisture content of 0.34–0.73 (w/w in w.b.) (Baik and Mittal 2003a). A linear relationship was observed between density and moisture content:

$$\rho = -474\,M + 1400 \quad (R^2 = 0.961) \tag{6.1}$$

where, $M$ is moisture content in w.b. (w/w) and $R^2$ is the coefficient of determination.

Kawas and Moreira (2001) studied the bulk and solid densities and porosity of tortilla chips during frying. The bulk density decreased from 880 kg/m$^3$ to 580 kg/m$^3$ after 60 s of frying as the volume of the chips increased due to an increase in puffiness during frying (Table 6.1).The solid density and porosity of raw tortilla chips were $1300 \pm 20$ kg/m$^3$ and $0.32 \pm 0.01$, respectively. The values of density and porosity were functions of frying time. The results showed that bulk density decreased, solid density remained constant and porosity increased during frying. The thickness of tortilla chips increased about 40% after frying as a result of the expansion caused by increase in porosity. Most of the changes in density occurred after 5–15 s of frying when most of the water evaporated from the chip. The solid density of tortilla chips fried for 60 s was $1300 \pm 20$ kg/m$^3$, and the porosity was $0.55 \pm 0.03$. At the initial stage of frying, the tortilla chips absorbed oil and lost water rapidly due to the

**TABLE 6.1**
**Density and Porosity of Tortilla Chips During Frying at 190°C in Soybean Oil**

| Time (s) | Bulk density (kg/m$^3$) | Solid density (kg/m$^3$) | Porosity |
|---|---|---|---|
| 5 | $880 \pm 70$ | $1300 \pm 20$ | $0.32 \pm 0.01$ |
| 10 | $970 \pm 70$ | $1270 \pm 30$ | $0.30 \pm 0.02$ |
| 15 | $790 \pm 90$ | $1280 \pm 20$ | $0.37 \pm 0.02$ |
| 20 | $650 \pm 50$ | $1290 \pm 20$ | $0.49 \pm 0.02$ |
| 25 | $540 \pm 70$ | $1310 \pm 20$ | $0.58 \pm 0.02$ |
| 30 | $520 \pm 90$ | $1280 \pm 10$ | $0.59 \pm 0.01$ |
| 45 | $540 \pm 70$ | $1300 \pm 10$ | $0.58 \pm 0.03$ |
| 60 | $580 \pm 60$ | $1300 \pm 20$ | $0.55 \pm 0.03$ |

Adapted from Kawas and Moreira (2001).

large surface area of the chips and the large particle size of masa. Tortilla chips had a slightly puffed structure due to the formation of gas cells during frying (Lee 2003).

Type of the frying medium (sunflower oil and shortening) did not affect the density of pork meat, whereas the density was lower when the frying temperature increased (Table 6.2). Density diminished with the increase in frying time, which was attributed to water loss and oil uptake (Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz 2006). The bulk density of fresh pork meat ranged between 1082.3 kg/m$^3$ and 1099.7 kg/m$^3$. After 120 min of frying, bulk density values were 1038.3 ± 4.2 at 90°C, 1023.7 ± 10.8 at 100°C and 996.0 ± 14.1 kg/m$^3$ at 110°C.

The bulk density of chicken drum muscle slab decreased as moisture content decreased from its initial value to zero when fried at 120–180°C (Ngadi and Correia 1995). The following relationship was obtained using experimental data:

$$\rho_b = 761 + 208M - 38\,M^2 \qquad (R^2 = 0.803) \tag{6.2}$$

where $\rho_b$ is the bulk density and M is the moisture content in dry basis. Table 6.3 summarizes the values of bulk and solid densities of some typical fried foods.

### 6.2.3 Porosity

Porosity ($\varphi$), defined as the volume fraction of the air or the void fraction in the sample, is calculated as:

$$\varphi = 1 - \frac{\rho_b}{\rho_p} = \frac{V_v}{V_b} \tag{6.3}$$

**TABLE 6.2**
**Physical Properties of Pork Meat Slabs During Frying at Different Temperatures**

| Frying oil | T, °C | Time, min | ρ, kg/m³ | Cp, kJ/(kg K) | k, W/(mK) | $\alpha \times 10^7$, m²/s |
|---|---|---|---|---|---|---|
| Sunflower | 90 | 0 | 1090.0 ± 11.8 | 4.54 ± 0.23 | 0.79 ± 0.05 | 1.83 ± 0.04 |
| | | 60 | 1071.3 ± 3.1 | 3.54 ± 0.28 | 0.60 ± 0.06 | 1.41 ± 0.36 |
| | | 120 | 1038.3 ± 4.2 | 3.13 ± 0.11 | 0.59 ± 0.05 | 1.67 ± 0.16 |
| | 100 | 0 | 1099.7 ± 20.8 | 3.99 ± 0.40 | 0.65 ± 0.04 | 1.48 ± 0.07 |
| | | 60 | 1073.3 ± 39.3 | 3.35 ± 0.21 | 0.59 ± 0.02 | 1.64 ± 0.25 |
| | | 120 | 1023.7 ± 10.8 | 2.78 ± 0.11 | 0.56 ± 0.01 | 1.65 ± 0.01 |
| | 110 | 0 | 1082.3 ± 8.4 | 3.72 ± 0.19 | 0.68 ± 0.00 | 1.54 ± 0.10 |
| | | 60 | 1057.3 ± 17.1 | 3.17 ± 0.02 | 0.56 ± 0.04 | 1.83 ± 0.07 |
| | | 120 | 996.0 ± 14.1 | 2.77 ± 0.04 | 0.35 ± 0.00 | 1.63 ± 0.25 |
| Shortening | 100 | 0 | 1090.3 ± 11.6 | 4.62 ± 0.20 | 0.62 ± 0.04 | 1.63 ± 0.20 |
| | | 60 | 1042.0 ± 13.0 | 3.76 ± 0.19 | 0.56 ± 0.04 | 1.12 ± 0.11 |
| | | 120 | 1030.7 ± 10.6 | 3.41 ± 0.27 | 0.53 ± 0.03 | 1.15 ± 0.11 |

Modified from Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz (2006).

**TABLE 6.3**
**Density of Some Typical Fried Foods**

| Product | Oil type | Temperature,°C | $\rho_b$, kg/m$^3$ | $\rho_s$,kg/m$^3$ | Reference |
|---|---|---|---|---|---|
| Donut, raw/fried | Sunflower | 180 | 526/340 | – | Velez-Ruiz and Sosa-Morales (2003a) |
| | | 190 | 551/333 | – | |
| | | 200 | 504/332 | – | |
| Sweet-potato | Canola | 170 | 1180–1270 (raw, varied due to pretreatments) | 1026–1160 (raw) | Taiwo and Baik (2007) |
| | | | 760–940 (fried) | 1190–1280 (fried) | |
| Chickpea flour suspension | Groundnut | 175 | 1114 (raw) | – | Bhat and Bhattacharya (2001) |
| | | | 219–366 (fried) | – | |
| Tofu (not fried) | – | Moisture content: 0.34–0.73 wb | 1053–1251 | – | Baik and Mittal 2003a |
| Tortilla chips | Soybean | 190 | $880 \pm 3$ (raw) | $1300 \pm 11$ (raw) | Moreira, Palau, and Sun 1995; Moreira et al. 1995 |
| | | | $579 \pm 2$ (fried) | $1288 \pm 2$ (fried) | |

where $\rho_b$ is the bulk density, $\rho_p$ is the solid density, $V_v$ is the void volume, and $V_b$ is the bulk sample volume.

For restructured potato product fried at 170°C in soy oil (Rubnov and Saguy 1997), porosity ranged from 0.79 to 0.82. Porosity of French fries increased with oil temperature and sample thickness, and was higher for product fried with hydrogenated cottonseed oil (Krokida, Oreopoulou, and Maroulis 2000a). The porosity of raw tortilla chip was $0.32 \pm 0.02$ and increased during frying to $0.55 \pm 0.04$ (Moreira et al. 1995). Maximum pore expansion in tortilla chips occurred between 30 s and 40 s of frying (Rajkumar, Moreira, and Barrufet 2003). Higher initial moisture content provided increasing porosity in the product from 42.12 to 54.04%. Pores occupied 33.4 and 50.8% at the start and end of the frying, respectively. The steepest increase in pores occurred between 20 s and 40 s of frying due to considerable loss of tortilla mass. The mean pore size increased from 6.69 mm$^3$ to 17.23 mm$^3$ due to a decrease in oil absorption and increase in temperature.

Pore developments in deboned chicken breast meat during frying were investigated (Kassama and Ngadi 2004). The results indicated a positive trend of pore development in chicken meat as frying time and temperature increased. Frying temperature and time have significant influences on pore development. Peak pore fractions of 0.283 (after 360 s of frying), 0.238 (after 900 s of frying) and 0.220 (after 900 s of frying) at frying temperatures of 190°C, 180°C and 170°C, respectively, were observed (Kassama and Ngadi 2004). The pore structure of deep-fat-fried chicken meat samples at 170–190°C in liquid shortening was also studied (Kassama and Ngadi 2005a). The cumulative pore volumes decreased by 24% from 2.13 ml/g

to 0.51 ml/g, mean pore diameter from 1.17 μm to 0.25 μm, and with a corresponding porosity of 0.71 to 0.37 after 360 s of frying. The cumulative pore surface area of the control (raw sample) was 6.92 $m^2$/g compared with 8.24 $m^2$/g in samples fried for 360 s (Kassama and Ngadi 2005b).

Suspensions of chickpea flour are widely used in the preparation of oriental traditional snacks and sweets. The analysis of microstructure of the product indicated that there were large pores and vacuoles inside, whereas the outer surface remained fairly smooth, with fewer smaller pores (Bhat and Bhattacharya 2001). Further details on the microstructure of fried products are given in chapter 8.

## 6.3 THERMAL PROPERTIES

### 6.3.1 Specific Heat, Thermal Conductivity, and Thermal Diffusivity

For raw meat products, specific heat varied from about 3.40 kJ/kg K to 3.60 kJ/kg K (based on composition), and thermal conductivity from 0.412 W/m·K to 0.557 W/m·K (Moreira, Castell-Perez, and Barrufet 1999). The thermal diffusivity was $3.846 \times 10^{-7}$ $m^2$/s for sausages (15 ± 0.1 cm in length, 2 ± 0.1 cm in diameter) fried at 180°C in sunflower oil (Dincer and Yildiz 1996).

Chicken slabs (10.0 × 1.0 × 0.5 cm) were fried in sunflower oil at 130, 140, and 150°C, and the thermal diffusivities of the samples for each oil temperature measured at different frying times (Velez-Ruiz et al. 2002). This property showed an increasing trend during the first 3 min (at 150°C), 4 min (at 140°C), and 5 min (at 130°C), from $7.0 \times 10^{-8}$ to $1.5–1.7 \times 10^{-7}$ $m^2$/s, and smoothly decreased for the rest of the frying period (from $1.7 \times 10^{-7}$ to $1.3 \times 10^{-7}$ $m^2$/s). The average thermal diffusivity values at 130 and 140°C were practically identical (Table 6.4) (Velez-Ruiz et al. 2002).

The thermal diffusivity for the frying of pastry (light biscuit mix) with gellan gum edible film (2-mm thickness) in soybean liquid shortening at 150°C were $0.102 \times 10^{-6}$ $m^2$/s for the food and $0.156 \times 10^{-6}$ $m^2$/s for the film (Williams and Mittal 1999). The thermal conductivity was 0.351 W/m·K for the pastry and 0.607 W/m·K for the film.

Table 6.5 provides physical properties of donuts during frying (Velez-Ruiz and Sosa-Morales 2000). Thermal conductivity of donuts was almost constant (0.0968–0.0978 W/m·K) at 180–200°C during frying in sunflower oil. The specific

**TABLE 6.4**
**Thermal and Moisture Diffusivities of Fried Chicken Slabs in Sunflower Oil**

| Oil temperature, °C | n | $\alpha$, $m^2$/s $\times 10^7$ | $D_m$, $m^2$/s $\times 10^8$ | Heat transfer coefficient (h), W/($m^2$ K) |
|---|---|---|---|---|
| 130 | 59 | 1.458 ± 0.333 | 0.880 | 207.6 |
| 140 | 64 | 1.459 ± 0.251 | 1.299 | 223.3 |
| 150 | 95 | 1.478 ± 0.365 | 1.544 | 331.0 |

$\alpha$ = thermal diffusivity, n = number of data, $D_m$ = moisture diffusivity
Modified from Velez-Ruiz et al. (2002).

**TABLE 6.5**
**Physical Properties for Donuts During Frying in Sunflower Oil**

| Time (s)/180°C | $D_m$, m²/s | k, W/(m K) | Cp, kJ/(kg K) |
|---|---|---|---|
| 15–30 | $1.36 \times 10^{-6}$ | 0.0978 | 2.436 |
| 45–75 | $0.55 \times 10^{-6}$ | 0.0975 | 2.714 |
| 90–180 | $0.30 \times 10^{-6}$ | 0.0974 | 2.714 |
| Time (s)/190°C | | | |
| 15–30 | $1.43 \times 10^{-6}$ | 0.0972 | 2.165 |
| 45–75 | $0.60 \times 10^{-6}$ | 0.0968 | 2.539 |
| 90–180 | $0.33 \times 10^{-6}$ | 0.0972 | 2.728 |
| Time (s)/200°C | | | |
| 15–30 | $1.06 \times 10^{-6}$ | 0.0974 | 2.331 |
| 45–75 | $0.51 \times 10^{-6}$ | 0.0974 | 2.647 |
| 90–180 | $0.28 \times 10^{-6}$ | 0.0970 | 2.963 |

Modified from Velez-Ruiz and Sosa-Morales (2000).

heat varied slightly with oil temperature (2.714 kJ/kg·K at 180°C; 2.728 kJ/kg·K at 190°C; and 2.963 kJ/kg·K at 200°C) after 120 s of frying. There was an increase in the average thermal diffusivity (up to 120 s frying time) of donuts with frying temperature, i.e., $1.00 \times 10^{-7}$ m²/s at 180°C, $1.013 \times 10^{-7}$ m²/s at 190°C, and $1.089 \times 10^{-7}$ m²/s at 200°C (Velez-Ruiz and Sosa-Morales 2003a, 2003b).

Moreira et al. (1995) studied the thermal properties of tortilla chips fried in fresh soybean oil for different times at 190°C. The thermal conductivity of tortilla chips decreased from 0.23 to $0.09 \pm 0.01$ W/m·K (average thermal conductivity was 0.13 W/m·K for 60 s of frying) and specific heat from 3.36 to $2.19 \pm 0.03$ kJ/kg K. During frying, specific heat of tortilla chips varied from 2.82 kJ/kg K to 2.19 kJ/kg K, indicating that specific heat decreased due to decrease in moisture content and increase in oil content. Moreover, the specific heat decreased by decrease in oil heat capacity due to oil degradation. The values of thermal diffusivity for tortilla chips at different frying times did not change significantly. The average thermal diffusivity value was $9.11 \times 10^{-8}$ m²/s with standard deviation of $5.67 \times 10^{-9}$ m²/s (Moreira et al. 1995). Chips fried faster in fresh oil than in used frying oil. In addition, the chips absorbed more oil when fried in used oil (Moreira, Palau, and Sweat 1992b). The thermal diffusivity for frying in fresh oil was $1.321 \times 10^{-5} \pm 0.519 \times 10^{-5}$ m²/s, and for frying in used oil was $1.620 \times 10^{-5} \pm 0.576 \times 10^{-5}$ m²/s. The relationship between thermal conductivity ($k$) and moisture content ($M$ in % db) was expressed by Moreira, Palau, and Sweat (1992a) as;

$$k = 0.0795 \ \exp(0.0254\, M) \quad (R^2 = 0.881) \tag{6.4}$$

Tortilla chips were also fried at 150 and 190°C in partially hydrogenated soybean oil (Moreira et al. 1995). Moisture loss rate increased as temperature increased. The

effect of oil temperature on oil uptake was not significant during the first 15 s of frying, but the final oil content was higher for the chips fried at 190°C than at 150°C for 60 s. The variation of specific heat, thermal conductivity and thermal diffusivity during frying at 190°C for $\leq 60$ s were reported as 2.31–3.36 kJ/kg.K (average of 2.56 kJ/kg.K), 0.11–0.37 W/m·K and $8.22 \times 10^{-8}$ to $12.5 \times 10^{-8}$ m$^2$/s (average of $9.11 \times 10^{-8}$ m$^2$/s) respectively.

Thermal properties of tofu were determined at temperatures of 5–80°C (10–105°C for specific heat) and the moisture content range of 0.3–0.7 (w/w in w.b.) (Baik and Mittal 2003a). Thermal conductivity (0.24–0.43 W/m·K) and thermal diffusivity ($7.6 \times 10^{-8}$–$1.15 \times 10^{-7}$ m$^2$/s) were measured simultaneously using the dual-probe method, and specific heat (2.52–3.69 kJ/kg.K) with modulated differential scanning calorimetry. Specific heat of tofu increased with moisture content and tofu temperature. The suitable model for the variation of specific heat with moisture content and temperature was described as;

$$C_p = 2.055 + 1.064M + 1.596M^2 + 1.06\times10^{-3}T \quad (R^2 = 0.959) \tag{6.5}$$

where $M$ is moisture content in w.b., w/w, and $T$ is food temperature in degrees centigrade.

Predicted thermal conductivity values from the parallel model did not match well with the experimental values, and indicated a root mean square of error (RMS) of 0.119. The perpendicular model provided good predictions with a RMS of 0.0118. The suitable model is (Baik and Mittal 2003a):

$$k = 0.2112 + 8.943\times10^{-4}MT + 0.3077M^2 \quad (R^2 = 0.944) \tag{6.6}$$

Yano et al. (1978) reported thermal conductivity of frozen and fresh tofu as 0.49 and 0.30 W/m·K, respectively. Thermal conductivity of the tofu increased with increase in temperature and moisture content.

The thermal diffusivity values, reported by Baik and Mittal (2003a), are slightly lower than those ($1.1 \times 10^{-7}$–$1.3 \times 10^{-7}$ m$^2$/s) of the tofu with moisture content range of 0.52–0.80 (w/w, wb) and temperature range of 0–3°C reported by Kong, Miyawaki, and Yano (1980). Developed empirical model which has a coefficient of determination of 0.966 is given as (Baik and Mittal 2003a);

$$\alpha = (0.0816 - 0.05682M + 0.1164\,M^2 + 6.866\times10^{-4} \\ M^2T - 5.17\times10^{-6}M^2T^2)\times10^{-6} \tag{6.7}$$

Thermal diffusivity of $1.33\times10^{-7}$ m$^2$/s was obtained for meatballs frying, at $159 \pm 1$°C in beef shortening, by minimizing the RMS deviations between observed and simulated temperature histories (Ateba and Mittal 1994a). The thermal diffusivity value was 13% lower than the result ($1.52 \times 10^{-7}$ m$^2$/s) obtained by Huang and Mittal (1995) who measured the thermal diffusivities of meatballs fried at 120°C. This is possibly due to the differences in frying temperatures. Table 6.6 summarizes the values of specific heat, thermal conductivity and thermal diffusivity for some typical fried foods.

**TABLE 6.6**
**Thermal Properties of Some Typical Fried Foods**

| Product | Oil type | Temperature, °C | Cp, kJ/(kg K) | k, W/(m.K) | $\alpha \times 10^8$, m²/s | Reference |
|---|---|---|---|---|---|---|
| Chicken slab | Sunflower | 130–150 | – | – | 7–13 | Velez-Ruiz et al. (2002) |
| Donut | Sunflower | 180–200 | 2.16–2.96 | 0.097–0.098 | 10–10.9 | Velez-Ruiz and Sosa-Morales, (2003b) |
| French fries | Sunflower | 140–180 | 4.036 | 0.56 | – | Costa et al. (1999) |
| Meatball | Beef shortening | 159 | – | – | 13.3 | Ateba and Mittal (1994b) |
| Pastry dough | Liquid canola shortening | 150 | – | 0.351 | 10.2 | Williams and Mittal, (1999) |
| Pork meat | Sunflower | 90–110 at 120 min | 2.77–3.13 | 0.35–0.59 | 16.3–16.7 | Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz (2006) |
| Sausage | Sunflower | 180 | – | – | 384.6 | Dincer and Yildız (1996) |
| Tofu (not fried) | – | Moisture content: 0.3–0.7 wb | 2.52–3.69 | 0.24–0.43 | 7.6–11.5 | Baik and Mittal (2003a) |
| Tortilla chips | Soybean | 190 | 3.36–2.19 | 0.09–0.23 | 9.1 | Moreira et al. (1995) |

The type of frying medium affected all thermal properties of pork meat, whereas the thermal conductivity and diffusivity were lower, and specific heat was higher when fried in shortening than sunflower oil (Table 6.2) (Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz 2006). For all frying temperatures and for sunflower oil and shortening, specific heat and thermal conductivity decreased during frying. Thermal diffusivity also reduced during 60 s of frying, but then increased. This may be attributed to water loss and oil uptake. All thermal properties decreased with increase in frying oil temperature from 90–110°C.

### 6.3.2 Heat Transfer Coefficient

The relationship between heat transfer coefficient and the turbulent flow behavior of vapor bubbles around the product surface was studied by Baik and Mittal (2002). The turbulence created by the bubbles decreases the stagnant liquid film thickness, thus increasing the convective heat transfer coefficient. In most frying studies, the convective heat transfer coefficient was indirectly measured using heat flux determination (Mittelman, Mizrahi, and Berk 1984; Miller, Singh, and Farkas 1994; Huang and Mittal 1995; Tseng, Moreira, and Sun 1996). To simulate agitation by vapor bubbling, a metal piece was surrounded by a wet food in heated oil (Costa et al. 1999). However, the flow pattern closer to the top surface of the metal was not the same as in frying. The bubbles from the bottom surface of the food, above the metal piece, flowed sideways to the bottom edge, and then flowed upward to the oil surface. Direct measurements were made by Costa et al. (1999) and by Hubbard and Farkas (1999; 2000), where an average convective heat transfer coefficient was determined for the food during frying. In direct measurement, convective heat transfer coefficient at different product surfaces was not quantified because simultaneous heat and mass transfer made the application of energy balance more complicated. Hence, indirect measurement with a heat flux-meter is more popular than direct measurement.

The convective heat transfer coefficient increased with oil temperature for chicken strips (Velez-Ruiz et al. 2002) (Table 6.4). This agreed with the report by Miller, Singh, and Farkas (1994) that the corresponding convective heat transfer coefficient for canola, corn, palm, and soybean oils varied from 250 $W/m^2{\cdot}K$ to 276 $W/m^2{\cdot}K$. For meat patty frying, convective heat transfer coefficient varied from 250 $W/m^2{\cdot}K$ to 300 $W/m^2{\cdot}K$ (Hallstrom 1979). It was reported as 300–700 $W/m^2{\cdot}K$ for meat patties at 190°C in hydrogenated oil (Dagerskog and Sorenfors 1978). For cylindrical shape potato products, convective heat transfer coefficient was 150–165 $W/m^2{\cdot}K$ at 50–100°C (Califano and Calvelo 1991). Convective heat transfer coefficient value reduced as the oil degraded. It was 282 $W/m^2{\cdot}K$ for fresh soybean oil and 261 $W/m^2{\cdot}K$ for used oil at 188°C (Miller, Singh, and Farkas 1994). Moreover, it was 285 $W/m^2{\cdot}K$ for frying of tortilla chips at 190°C in fresh soybean oil and 273 $W/m^2{\cdot}K$ for used oil (Moreira, Palau, and Sweat 1992a). According to Tseng, Moreira, and Sun (1996), convective heat transfer coefficient decreased nonlinearly from 274 $W/m^2$ to 250 $W/m^2{\cdot}K$ as oil quality decreased.

The convective heat transfer coefficient values were measured at the top and bottom surfaces of a tofu disc during frying at 147–172°C in liquid canola oil shortening (Baik and Mittal 2002). The direct measurement was based on the energy balance

between convective heat from oil to the product surface, and the summation of sensible heat for temperature increase in the product and latent heat for evaporation. In the presence of vapor bubbling, convective heat transfer coefficient values at the top surface of the tofu disc ($h_{max}$: 722–827 $W/m^2K$) were higher than those at the bottom surface ($h_{max}$: 644–724 $W/m^2K$).

The convective heat transfer coefficient during frying is affected by bubble flow direction, velocity, bubble frequency, and the magnitude of oil agitation. Bubbles that formed at the top of the product surface escaped upward, providing greater oil agitation. The ones leaving the lateral surfaces moved upward along the lateral surface, promoting a different type of agitation. Bubbles that left the bottom surface coalesced before flowing against the tofu surface to the edges, and then moved to the top oil surface along the lateral surfaces (Baik and Mittal 2002).

The convective heat transfer coefficients at the top and bottom surfaces of potatoes during deep-fat frying were determined within the temperature range of 150–190°C (Sahin, Sastry, and Bayindirli 1999a). It was in the range of 300–335 $W/m^2$ °C for the top surface. It varied between 450 $W/m^2$ °C and 480 $W/m^2$ °C before crust formation and between 70 $W/m^2$ °C and 150 $W/m^2$ °C after the crust formation for the bottom surface.

Oil temperature, frying time and location had significant effects on the convective heat transfer coefficient. For all temperatures, convective heat transfer coefficient values at the top surface were higher (8–14%) than those at the bottom surface. For whole tofu, mean convective heat transfer coefficient values increased with oil temperature. For the period when the convective heat transfer coefficient value was maximal, mean h values were similar at 147°C and 160°C, but higher at 172°C, suggesting an exponential relationship between oil temperature and maximum h above 160°C (Baik and Mittal 2002). The maximal h values at 147°C, 160°C, and 172°C were 722, 743, and 826 $W/m^2K$, respectively. These values were comparable with 600, 645, and 895 $W/m^2K$ recorded for a potato cylinder (diameter: 16 mm, height: 90 mm) during frying at 120°C, 150°C, and 180°C in canola oil (Hubbard and Farkas 2000). The maximum heat fluxes during the tofu disc frying were 36022, 41234, and 50807 $W/m^2$ at the top surface, and 29480, 35282, and 38170 $W/m^2$ at the bottom surface at 147°C, 160°C and 172°C, respectively (Baik and Mittal 2002).

Before vapor release, natural convection dominates the convective heat transfer coefficient in the frying process. This period is, however, very short. For frying at 160°C and 172°C, vapor bubbles were visible within 10 s and 5 s, respectively, after immersion of the tofu disc. However, significant amounts of bubbles were released after 30 s of frying at 147°C. Thus, at the beginning of frying, lower convective heat transfer coefficient value was observed at the top surface compared with the bottom surface. Lower oil temperature resulted in a longer period of natural convective heat transfer. Bubbling promotes convective heat transfer by agitating the oil, but bubbles may form an insulation layer depending on their flow direction, velocity, and bubbling frequency (Baik and Mittal 2002). The convective heat transfer coefficient for meatballs was determined by the transient temperature measurement method to be 284.6 $W/m^2K$, for frying at $159 \pm 10$°C in beef shortening (Ateba and Mittal 1994a).

Budzaki and Seruga (2005a) used the dough ball of wheat flour with different amounts of whole potato flour having a diameter of 2.5 cm as a sample for

the determination of convective heat transfer coefficient. The convective heat transfer coefficient was the highest at the beginning of frying at 160–190°C in soybean oil (197.25 ± 1.39 to 774.88 ± 3.90 W/m$^2$K) and the lowest in the case of setting up a uniform period of water migration from the sample, which corresponded to surface temperatures slightly higher than 100°C (94.22 ± 0.33 to 194.84 ± 0.91 W/m$^2$K). Addition of whole potato flour in dough considerably decreased the convective heat transfer coefficient regardless of the frying oil temperature.

The convective heat transfer coefficient was 282 ± 36 W/m$^2$K during frying of potato slices of 8.5 × 8.5 × 70 mm at 170°C sunflower oil (Yildiz, Palazoglu, and Erdogdu 2005). In another study by Costa et al. (1999) for potato frying at 140–180°C in sunflower oil, the convective heat transfer coefficient increased with frying time up to a maximum of 594 ± 38 W/m$^2$K at 140°C and 750 ± 59 W/m$^2$K at 180°C for crisps; 443 ± 32 W/m$^2$K at 140°C and 650 ± 7 W/m$^2$K at 180°C for French fries, and then decreased. The h values, in the absence of bubbling, were 436 ± 40 W/m$^2$K at 140°C and 416 ± 27 W/m$^2$K at 180°C for crisps; and 353 ± 32 W/m$^2$K at 140°C and 389 ± 15 W/m$^2$K at 180°C for French fries. Thus, the convective heat transfer coefficient values were up to two times larger than those obtained in the absence of vapor bubbling, and varied with the water loss rate, showing a maximum value close to the time when the maximum water rate was reached. Sahin, Sastry, and Bayindirli (1999b) measured convective heat transfer coefficient value using aluminum wool with potato mash slabs (0.05 × 0.05 × 0.003 m) during frying in sunflower oil, and obtained an increase in h from 90 W/m$^2$K to 200 W/m$^2$K with the increase in oil temperature within the range of at 150°C to 190°C.

Hubbard and Farkas (2000) determined the convective heat transfer coefficient for potato cylinders (1.6-cm diameter and 9-cm length) during frying in canola oil at 120–180°C. As oil temperature increased, the maximum convective heat transfer coefficient over the frying process also increased. The maximum values of 610, 650 and 890 W/m$^2$K were found at oil temperatures of 120, 150, and 180°C, respectively. The convective heat transfer coefficient value at the beginning of frying (approximately 300 W/m$^2$K) matched well with the value reported by Miller, Singh, and Farkas (1994) for the non-boiling phase of frying in soybean oil at 180°C (281 W/m$^2$K). The highest convective heat transfer coefficient values at 180°C oil temperature were between 100 W/m$^2$K and 200 W/m$^2$K.

The convective heat transfer coefficient values for breaded cheese bars, during frying at 160–180°C in sunflower oil were 152–187 W/m$^2$K (Velez-Ruiz et al. 2005). In this study, Gouda and Manchegu cheeses were used. Vijayan and Singh (1997) reported a convective heat transfer coefficient value of 300–500 W/m$^2$·K for frying of frozen foods. The h for donuts was 158.6 at 180°C, 269.5 at 190°C and 296.8 W/m$^2$·K at 200°C (Velez-Ruiz and Sosa-Morales 2003b). Table 6.7 summarizes h values for the fried foods discussed in this section.

## 6.4 MASS TRANSFER PROPERTIES

Chicken nuggets were deep-fat fried at three temperatures (150, 170 and 190°C) in a liquid shortening for 1–4 min (Ngadi, Dirani, and Oluka 2006). There was rapid moisture loss from the breading portion within the first 2 min of frying. Values of

**TABLE 6.7**
**Convective Surface Heat Transfer Coefficient Values During Deep-fat Frying of Foods**

| Product | Shape | Dimensions | h, W/(m² K) Non-boiling | h, W/(m² K) Boiling | Oil Temperature, °C, oil type | Reference |
|---|---|---|---|---|---|---|
| Breaded cheese | Bar | – | 152–187 | – | 160–180, sunflower | Velez-Ruiz, Costa-Jimenaz, and Sosa-Morales (2005) |
| Crisps, French fries | Slices | – | 416–436, 353–389 | 594–750, 443–650 | 140–180, sunflower oil | Costa et al. (1999) |
| Dough (wheat + potato flour) | Sphere | 2.5 cm diam. | 197.2 ± 1.4 | 774.9 ± 3.9 | 160–190, soybean oil | Budzaki and Seruga (2005a) |
| French fries | Slices | 8.5 × 8.5 × 70 mm | 282 ± 36 | – | 170, sunflower oil | Yildiz, Palazoglu, and Erdogdu (2005) |
| Meatball | Sphere | 4.7 cm diam. | 284.6 | – | 160 | Ateba and Mittal (1994a) |
| Meat patties | Disc | 11 mm thick | – | 500 ± 200 | 160, hydrogenated | Dagerskog and Sorenfors (1978) |
| Meat patties | Disc | 10 mm thick | 250–300 | – | 130–190, hydrogenated | Hallstrom, (1979) |
| Potato | Cylinder | 16 mm diam. 9 cm height | 300 | 610–890 | 120–180, canola | Hubbard and Farkas (2000) |
| Potato | Cylinder | – | 150–165 | – | 50–100 | Califano and Calvelo (1991) |
| Potato mash + Al wool | Slices | 5 × 5 × 0.3 cm | 90–200 | – | 150–190, sunflower | Sahin, Sastry, and Bayindirli (1999) |
| Tofu | Disc | 57 mm diam. 10 mm thick | – | 722* | 147, hydrogenated | Baik and Mittal (2002) |
| | | | – | 743 | 160 | |
| | | | – | 826 | 172 | |

* Maximum h for boiling stage

Modified from Farinu and Baik (2005).

moisture diffusivity were ranged from $20.93 \times 10^{-10}$ to $29.32 \times 10^{-10}$ $m^2/s$. The activation energy was 8.04 kJ/mol. Moisture loss profiles in the breading and core portions of the product were significantly different. Moisture loss in the core region changed only slightly in the early stages of frying, but increased afterwards in chicken meat (Ngadi, Dirani, and Oluka 2006). Effective diffusivity ranging from 5.4 to $6.9 \times 10^{-9}$ $m^2/s$ and activation energy of 20 kJ/mol was obtained for frying of chicken meat (Kassama and Ngadi 2004). Changes in pore structure influenced the moisture diffusivity and oil uptake. Moisture transfer increased because 84% of the pores were capillary (Kassama and Ngadi 2004, 2005a).

Effective moisture diffusivity in chicken drum muscle samples ($65 \times 25 \times 3$ mm) during frying ranged between $1.32 \times 10^{-9}$ and $1.64 \times 10^{-8}$ $m^2/s$ for moisture range of 0.06 to 0.33 (w/w in db) (Ngadi and Correia 1995). It increased with increasing frying oil temperature from 120°C to 180°C. The activation energy of 24 kJ/mol was independent of muscle moisture content (Ngadi and Correia 1995). The model for the moisture diffusivity was:

$$D_m = 8.35 \times 10^{-6} \exp(-2930/T_f - 0.561M + 0.092M^2) \tag{6.8}$$

Where, $M$ is the moisture content in db and $T_f$ is frying oil temperature.

Moisture diffusivity is generally higher in foods having higher porosity due to an increase in moisture mobility. $D_m$ values for fried chicken slabs at various temperatures are given in Table 6.4. The values varied from 0.88 to $1.544 \times 10^{-8}$ $m^2/s$ for oil temperatures of 130–150°C with activation energy of 34.4 kJ/mol (Velez-Ruiz et al. 2002). Table 6.8 shows the moisture diffusivity values and activation energies of typical fried foods.

Gel strength of pre-fried product, expressed by deformability modulus, was 37–127 kPa. Change in gel strength affected the $D_m$ of restructured potato, which was $3.31–1.58 \times 10^{-9}$ $m^2/s$ when fried at 170°C using soybean oil (Pinthus et al. 1997). The relationship between the moisture diffusivity and modulus of deformability was given by:

$$D_m = 3.43 \times 10^{-8} E_d^{-0.64} \qquad (R^2 = 0.95) \tag{6.9}$$

where, $E_d$ is the modulus of deformability, kPa.

During potato frying, the water loss rate increased, water started vaporizing, and bubbles flowed through the oil. The water loss rate increased until complete drying of the potato surface, and then decreased till the end of bubbling, with maximum values dependent on oil temperature and potato geometry (Costa et al. 1999).

Pedreschi, Hernandez, and Figueroa (2005) studied the effects of blanching and air drying on moisture diffusivity of potato slices (2.5-cm thick) during frying in sunflower oil at 120–180°C. The variable diffusivity model provided better predictions than the constant diffusivity model. The diffusivity increased with frying time and temperature, and the trend was similar for control and blanched slices (Table 6.9). Activation energies for constant diffusivity were 4.5, 4.7 and 6.0 kJ/mol for the control, blanched and dried potato chips, respectively. Moisture diffusion decreased as oil content increased. This was due to the hydrophobic character of fat,

**TABLE 6.8**
**Moisture Diffusivity ($D_m$) Values and Activation Energies of Some Typical Fried Foods**

| Products | Oil type | $D_m \times 10^{-10}$, m²/s | Activation energy, kJ/mol | Temperature,°C | References |
|---|---|---|---|---|---|
| Chicken nuggets | Liquid shortening | 20.93—29.32 | 8.04 | 150—190 | Ngadi, Dirani, and Oluka (2006) |
| Chicken drum muscles | – | 13.2—164 | 24 | 120—180 | Ngadi and Correia (1995) |
| Chicken meat | Liquid shortening | 54—69 | 20 | 170—190 | Kassama and Ngadi (2004) |
| Chicken slab | Sunflower | 88—154.4 | 34.4 | 130—150 | Velez-Ruiz et al. (2002) |
| Krostula dough | Soybean | 9.32—11.35 | 5.5 | 160—190 | Budzaki and Seruga (2005b) |
| Meatball | Beef shortening | 800 | – | 160 | Ateba and Mittal (1994b) |
| Potato slice | Sunflower | 35.5—348 | 4.5–6 | 120—180 | Pedreschi, Hernandez, and Figueroa (2005) |
| Potato slice | Shortening | 80—135 | 24.2 | 145—185 | Rice and Gamble (1989) |
| Samosa | – | 262—342 | | 155—185 | Indira, Latha, and Prakash (1999) |
| Tofu | Liquid shortening | 8.2—11.9 | 39.5 | 147—172 | Baik and Mittal (2005) |
| Tortilla chips | Soybean | 540.8—934.8 | – | 150—190 | Moreira, Palau, and Sun (1995); Moreira et al. (1995) |

**TABLE 6.9**
**Moisture Diffusivity ($D_m$) Values for Frying of Potato Slices**

| Oil Temperature, °C | 120 | 150 | 180 |
|---|---|---|---|
| **Constant $D_m$, m²/s** | | | |
| Control | $3.86 \pm 0.05 \times 10^{-9}$ | $9.86 \pm 0.57 \times 10^{-9}$ | $1.72 \pm 0.02 \times 10^{-8}$ |
| Blanched at 85°C, 3.5 min | $3.55 \pm 0.06 \times 10^{-9}$ | $9.76 \pm 0.47 \times 10^{-9}$ | $1.71 \pm 0.01 \times 10^{-8}$ |
| Blanched and air dried to 60% mc db | $4.53 \pm 0.06 \times 10^{-9}$ | $1.28 \pm 0.07 \times 10^{-8}$ | $3.48 \pm 0.05 \times 10^{-8}$ |
| **Variable diffusivity model, $D_o$ and b values ($D_m = D_o(1+D_o\, t/l^2)^b$), l = half slab thickness, m** | | | |
| Control | $1.29 \pm 0.20 \times 10^{-10}$<br>$4.51 \pm 1.07$ | $4.17 \pm 1.13 \times 10^{-9}$<br>$3.16 \pm 1.35$ | $7.14 \pm 1.06 \times 10^{-9}$<br>$3.07 \pm 0.83$ |
| Blanched at 85°C, 3.5 min | $2.05 \pm 0.67 \times 10^{-10}$<br>$1.82 \pm 1.28$ | $3.89 \pm 0.67 \times 10^{-10}$<br>$3.33 \pm 0.88$ | $7.77 \pm 2.42 \times 10^{-9}$<br>$2.75 \pm 1.56$ |
| Blanched and air dried to 60% mc db | $2.67 \pm 0.54 \times 10^{-10}$<br>$1.66 \pm 0.82$ | $5.55 \pm 0.46 \times 10^{-10}$<br>$3.05 \pm 0.64$ | $1.13 \pm 0.10 \times 10^{-9}$<br>$4.69 \pm 0.60$ |

Modified from Pedreschi, Hernandez, and Figueroa (2005).

which imposed a resistance to the flow of water. Moisture diffusivity increased as the potato slices dried during frying. Reduced moisture content formed more porous microstructure, which made water diffusion easier. Moisture diffusivity increased as the moisture content decreased during frying independent of the pretreatment of potato slices. As the frying temperature increased, the slices absorbed less oil. Moisture diffusivity increased with frying time and temperature, and was found to be dependent mainly on the slice moisture content.

Moisture diffusivity for restructured potato product, fried at 170°C in soybean oil, ranged from $0.87 \times 10^{-9}$ m²/s to $1.07 \times 10^{-9}$ m²/s (Rubnov and Saguy 1997). Added fructose reduced moisture diffusivity of pre-fried samples from $2 \times 10^{-9}$ m²/s to $1.26 \times 10^{-9}$ m²/s. For potato slice frying, the $D_m$ values were $0.8 \times 10^{-8}$ at 145°C, $1.10 \times 10^{-8}$ at 165°C and $1.35 \times 10^{-8}$ m²/s at 185°C with activation energy of 24.2 kJ/mol (Rice and Gamble 1989).

Baik and Mittal (2005) studied the moisture diffusivity of tofu and obtained the following model:

$$D_m = 9.5 \times 10^{-4} \exp(-4750 / T_{ab} + 0.011M) \tag{6.10}$$

where $T_{ab}$ is the product temperature in K, and $M$ is the moisture content in db (w/w). The effective activation energy, calculated through the proposed model for tofu frying, was 39.5 kJ/mol. This activation energy was based on local product temperature ($T_{ab}$ in K). The apparent $D_m$ values from the model for the average product temperature of 67.1–76.4°C and average moisture content of 0.702–0.685 (db) during frying at 147–172°C were $0.82–1.19 \times 10^{-9}$ m²/s.

Mittal (1999) reported the $D_m$ values of different fried foods. Dincer and Yildiz (1996) studied moisture diffusion in sausages (2 cm in diameter and 15 cm in length) during frying in sunflower oil at 180°C. Based on moisture profiles in the product, $D_m$ was $1.312 \times 10^{-7}$ m²/s.

In another study, mass transfer of chips was determined as a function of oil degradation. Chips fried faster in fresh rather than in used partially hydrogenated soybean oil (Moreira, Palau, and Sweat 1992a, 1992b). The variation of moisture content of tortilla chips (M, % db) with time (t, s) in the case of frying in fresh and used oils are given in Equation 6.11 and Equation 6.12, respectively;

$$M = 49.962\ \exp(-0.1976t) + 3.0688 \tag{6.11}$$

$$M = 54.590\ \exp(-0.152t) + 3.2586 \tag{6.12}$$

Moisture diffusivity values for tortilla chips fried in fresh and used hydrogenated soybean oil were $8.897 \times 10^{-6} \pm 1.773 \times 10^{-7}$ m²/s and $6.851 \times 10^{-6} \pm 6.418 \times 10^{-7}$ m²/s, respectively (Moreira, Palau, and Sun 1995; Moreira et al. 1995). The diffusivity of oil ($D_{oil}$) was $1.321 \times 10^{-5} \pm 0.519 \times 10^{-5}$ m²/s for fresh oil, and $1.620 \times 10^{-5} \pm 0.576 \times 10^{-5}$ m²/s for used oil. The moisture diffusivity was larger at 190°C ($9.348 \times 10^{-8}$ m²/s) than at 150°C ($5.408 \times 10^{-8}$ m²/s). The surface mass transfer coefficient was 0.00187 m/s (Moreira, Palau, and Sun 1995).

Moisture diffusivity values for meatballs (beef, 4.7 cm diameter, 60 g mass) during frying were estimated by minimizing the RMS of deviations between observed and predicted moisture histories (Huang and Mittal 1995). For frying meatballs in beef shortening at 160°C, $D_m$ was $8.0 \times 10^{-8}$ m²/s. Fat diffusivity in the meatball was $0.287 \times 10^{-7}$ m²/s, while fat conductivity followed Eyring's model with a frequency factor of $0.137 \times 10^{-6}$ m/s·K and activation energy of 2.70 kJ/mol (Ateba and Mittal 1994a). The average fat content increased by 3% during the fat-absorption period. Moreira, Palau, and Sweat (1992b) observed fat absorption by tortilla chips during the first few seconds of frying. They reported a fat diffusivity of $1.321 \times 10^{-5}$ m²/s.

A fat conductivity (KL) value, which gives a measure of the rate at which fat is transported by capillary flow, was determined to be $0.300 \times 10^{-4}$ m/s (Ateba and Mittal 1994a). The fat conductivity was affected by the viscosity and density of the fat. Because viscosity and density are temperature-dependent, the temperature dependency of fat conductivity was also considered:

$$\mathrm{KL} = 0.137 \times 10^{-6}\,\mathrm{T_{ab}}\exp(-325/\mathrm{T_{ab}}) \tag{6.13}$$

where $T_{ab}$ is absolute temperature. The equilibrium fat content was 0.57 (w/w db).

Ateba and Mittal (1994a) reported the fat diffusivity of beef meatballs during frying as $0.287 \times 10^{-7}$ m²/s. This is comparable with the values of $1.321 \times 10^{-5}$ m²/s in tortilla chips (Moreira, Palau, and Sweat 1992a) and $4.9 \times 10^{-8}$ m²/s and $12.2 \times 10^{-8}$ m²/s in restructured potato product (Rubnov and Saguy 1997).

Moisture diffusivity values for the food and the film were $0.33 \times 10^{-7}$ m²/s and $0.25 \times 10^{-7}$ m²/s, respectively for the frying of pastry (light biscuit mix) with gellan gum edible film (2-mm thickness) in canola liquid shortening at 150°C (Williams and Mittal 1999). The $D_m$ of film increased with the increase in film thickness. Fat diffusivities were $0.103 \times 10^{-8}$ m²/s for the food and $0.604 \times 10^{-9}$ m²/s for the 2-mm gellan gum film during frying.

The moisture diffusivity ranged from $1.41 \times 10^{-7}$ m$^2$/s to $3.86 \times 10^{-6}$ m$^2$/s for donuts frying in sunflower oil at 180–200°C (Velez-Ruiz and Sosa-Morales 2003b). The higher moisture diffusivity was at the initial frying stage and high oil temperature, whereas lower diffusivity was at final processing conditions and at 180°C. An average moisture diffusivity of $1.285 \times 10^{-6}$ m$^2$/s was obtained during the first 30 s of frying.

The effective oil diffusivity values of Krostula dough in the frying time range of 0–210 s at temperatures of 160, 170, 180 and 190 ± 1°C in soybean oil were 0.932, 1.135, 1.094 and $1.054 \times 10^{-9}$ m$^2$/s, respectively and the activation energy was 5.5 kJ/mol (Budzaki and Seruga 2005b).

## 6.5 TEXTURAL PROPERTIES

Due to water evaporation and protein denaturation, structural changes in chicken slices were reflected as dimensional changes (Velez-Ruiz et al. 2002). The viscoelastic behavior of potato strips during frying was examined by Krokida, Oreopoulou, and Maroulis (2000a). Maximum stress, maximum strain, elasticity modulus and viscoelastic exponents were significantly affected by frying conditions. Maximum stress and corresponding strain increased during frying and with decrease in frying temperature. Potatoes lost their elasticity during frying.

Textural properties of potato chips varied with the frying medium. Potato chips fried in hydrogenated oil had the lowest value for breaking strength and a greater amount of fat absorption compared with refined soybean and groundnut oils (Rani and Chauhan 1995).

Unblanched potato strips were crispier than blanched chips, and had higher values of maximum force at break and lower values of deformation at break (Pedreschi 2004). The study on potato crisps showed that fat content and texture of potato crisps were influenced by the type of frying oil used. A frying temperature <170°C markedly reduced the hardness of potato crisps. A decrease in frying temperature of rapeseed oil from 190°C to 170°C had no influence on the texture of potato crisps (Kita, Lisinska, and Golubowska 2007).

Tortilla chips became harder within 30 s of frying, and then crunchy until the end of frying as moisture decreased (Kawas and Moreira 2001). The crunchiness of the chip increased during frying. In general, the crispness of tortilla chips increased as frying time increased (Moreira et al. 1995). The force needed to break the tortilla chip increased from 2 N to about 11 N after 5 s of frying. It reached a highest value of 13 N after 10 s, and reached 6.5 N after 30 s of frying. The energy required to break the chip increased from 0.004 N·m to 0.013 N·m after 5 s, and remained constant at around 0.0025 N·m after 30 s of frying (Moreira et al. 1995).

Specific shear force and toughness of onion ring coatings were perceived as indicators of the hardness and chewiness of coatings, respectively (Ling et al. 1998). Specific shear force and toughness increased with frying temperature and frying time.

The viscoelastic properties of tofu were characterized using the stress relaxation test after frying at 147–172°C for 0–5 min (Baik and Mittal 2006). The results were expressed by a model with two Maxwell elements and a residual spring in parallel. Each elastic modulus and relaxation time followed zero-order reaction kinetics.

The Arrhenius type of temperature dependency was applied for the modeling of the reaction rate constant. The activation energies for the viscoelastic properties were 100–149 kJ/mol.

Development of an external oily and crispy crust is a major structural transformation occurring during frying of potatoes due to high temperature (160–190°C) and oil infiltration (Pedreschi, Aguilera, and Pyle 2001). By softening of the middle lamella between cells, starch gelatinization inside cells and dehydration, crust formation in fried potatoes is the result of changes in the original structure of the potato tissue after exposure to hot oil (about 170–180°C). Higher frying temperatures accelerated cooking of the core and hardening of the crust. A finished fried potato strip became a composite structure made of a hard crust region and soft core region.

Changes in the shape of the force–distance curves during frying permitted the kinetics of texture development and structural changes in potato strips during frying to be evaluated. Frying shows an initial stage where whole tissue softens, the core cooks and crust formation starts; at a later stage, the crust develops and hardens progressively. Higher frying temperatures accelerated cooking of the core and hardening of the crust, resulting in French fries with harder crusts. A finished fried potato strip became a composite structure made of a hard crust region and a soft core region (Pedreschi, Aguilera, and Pyle 2001).

Physical properties were studied in the crust region of a restructured potato product undergoing deep-fat frying (Pinthus, Weinberg, and Saguy 1995). Deformability modulus of raw material, ranging from 37 kPa to 137 kPa, markedly affected moisture content and oil uptake by the product and its crust. It also affected crust thickness at a frying time of 5 min. Lower deformability modulus promoted thicker crust ranging from $327 \pm 17$ μm to $650 \pm 29$ μm. Crust porosity decreased throughout frying, and was markedly affected by lower gel strength. Crust yield strength was affected by frying time and deformability modulus of the raw material. Crust oil uptake stopped when crust yield strength reached to a critical value of 210–240 kPa. Oil uptake in the crust ranged approximately from 35 to 38% after 1 min, and 60% to 85% after 5 min of frying (Pinthus, Weinberg, and Saguy 1995).

Crust formation in French fries started when the surface temperature reached approximately 103°C, and crust thickness increased linearly with the square root of frying time (Costa, Oliveira, and Boutcheva 1997). This increase was faster at the higher temperature of 180°C. The pore volume decreased during frying. Crust thickness of fried frozen French fries increased with frying time of up to 4 min. After the early stage of frying (1 min), crust thickness (347–359 μm) was not affected by restructured potato gel strengths. On the other hand, markedly thicker crusts (327–650 μm), were obtained for lower gel strengths in the later stages of frying (5 min). A slightly thinner crust was obtained at the highest gel strength examined. Deformability modulus markedly affected crust moisture content at a later frying stage (5 min), but had only a moderate effect on crust and overall moisture content for shorter frying times.

Mechanical properties of the crust of a fried starch-based material were determined by a puncture test and a three-point bend test. Puncture force and flexural strength of the crust increased with frying time and temperature, which was attributed to strengthening factors such as decreased moisture (Lima and Singh 2001).

The kinetics of crust formation and quality changes in meatballs during frying were evaluated (Ateba and Mittal 1994b). Crust thickness increased linearly with frying time, becoming darker and harder. It took about 9 min for the center temperature of sample to reach 70°C when the crust thickness was 1.84 mm. The increase in total crust color change was attributed to the high temperature and low moisture content of the product surface, which initiated browning reactions during crust formation. The increase in hardness (peak force) was thought to be due to heat denaturation of protein (Ateba and Mittal 1994b). Meatball firmness kinetics was modeled using peak force (PF) data obtained from the puncture test. The kinetics model for firmness was:

$$\mathrm{d(PF)/dt} = k(\mathrm{PF})^n \tag{6.14}$$

with $k$ and $n$ values of $5.39 \times 10^{-3}$ and 0.0013, respectively.

The penetration force on the fried meat crust increased with the frying time and oil temperature, indicating that the crust was harder when the process advanced, which is a typical characteristic of frying foods (Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz 2006). Pre-fried restructured potato gel strength, expressed by its deformability modulus, varied from 37 kPa to 127 kPa (Pinthus et al. 1997).

## 6.6 COLOR

The color of the fried potatoes and potato chips is one of the most significant quality factors of acceptance. The lightness (L) of potato chips increased during the early stages of frying, whereas it remained almost constant afterwards (Krokida et al. 2001). As the temperature of frying increased, for the same frying time, L decreased, giving equilibrium lightness values ranging from 74 to 78. Parameter "a" increased significantly during frying. As the temperature of frying increased, the "a" increased for the same frying time. The "a" increased with decrease in sample thickness, for the same frying time. Equilibrium "a" values increased with temperature increase, and its values were higher for smaller sample size. In general, higher "b" parameter values gave more yellow products, which is desirable for fried products. The "b" slightly increased with increase in temperature, and decreased with decrease in sample thickness (Krokida et al. 2001).

Three color parameters (L, a, b) of donuts were significantly correlated with frying time, showing an increasing redness (a) and a decreasing lightness (L) as a function of the process time (Velez-Ruiz and Sosa-Morales 2003a).

Color of fried onion rings was affected by frying temperature (Ling et al. 1998). Onion rings fried at 190°C had lower L (decreased lightness), higher "a" (increased redness), and lower "b" values (decreased yellowness) than onion rings cooked at 170°C. These color changes resulted from the increased rate of non-enzymatic browning (Maillard) reactions between proteins and reducing sugars at higher temperatures. Similarly, in coated chicken thighs and breasts decreased in L, increased in "a", and decreased in "b" with increasing frying temperature (Waimaleongora-Ek and Chen 1983). Similar color changes were reported for coated chicken parts with increasing frying time. Positive "a" values (redness) of onion rings also increased

with frying time whereas L and "b" did not change significantly with frying time (Ling et al. 1998).

The color changes of chickpea flour products during frying at 175°C in groundnut oil were described in terms of tristimulus values (brightness, hue and chroma) and yellowness, of which brightness decreased markedly; the color of the product changed from bright yellowish orange (raw batter) to dull orange (finished product) (Bhat and Bhattacharya 2001).

That frying induced surface browning was reflected in a decreasing lightness (L*) as well as the hue parameter (b*/a* value) for *Gulabjamun* (fried sweet product made with wheat flour and concentrated milk very popular in India). Increase in the hardness and firmness, followed zero-order reaction kinetics, whereas stiffness increase followed a first-order reaction. L* followed zero-order kinetics and a* and b* followed a first-order reaction. Activation energy was also obtained for the color and texture changes, which were in the range of 24.52–77.58 kJ/mol. It was 77.58, 62.34 and 24.52 kJ/mol for hardness, firmness and stiffness, respectively. Activation energies for L*, b*/a* and ΔE (color change) were 43.52, 31.34 and 28.66 kJ/mol, respectively. High correlations between color and texture parameters were observed, and it was concluded that L alone could be used to predict the firmness of deep-fat fried *Gulabjamun* balls (Kumar et al. 2006).

Color kinetics of tofu (extra firm variety) was studied during frying at 147–172°C. Lightness (L*) decreased exponentially from 85.5 to 68.0 with frying time, while redness (a*) and total color change (ΔE) increased from –1.17 to 6.72, and from 0 to 26.7, respectively. Yellowness (b*) increased from 18.8 to 34.5 and then decreased exponentially to a minimum of 29.4. All color parameters followed first-order kinetics. Temperature dependency of the reaction rate constant was modeled using the Arrhenius equation. The activation energy for color parameters was 76.0–165 kJ/mol (Baik and Mittal 2003b).

The change in pork meat color increased with the advance of frying time. For frying in sunflower oil, color was affected by frying temperature. A significant effect of frying medium was observed on the crust color changes, being lowest when shortening was utilized (Sosa-Morales, Orzuna-Espiritu, and Velez-Ruiz 2006).

Achieving optimal color and texture in French fries requires careful control of the unit operations that convert the raw potatoes into fries (Agblor and Scanlon 2000). Fries blanched by low-temperature long-time conditions (70°C, 10 min; 97°C, 2 min) had larger peak force, peak deformation and L* value than fries processed by standard conditions (85°C, 2 min). High-temperature short-time blanching (97°C, 2 min) increased L*, but decreased peak force. For drying, the color and textural quality of French fries processed by standard conditions (70°C, 10 min; 120°C, 11 min) were better than those processed by the drying alternatives (low temperature, long time (70°C, 10 min; 100°C, 15 min) and high temperature, short time (100°C, 20 min).

The variation of lightness (L*), redness (a*), yellowness (b*) and total color change (ΔE) of beef meatball crust followed first-order kinetics during frying (Ateba and Mittal 1994b). L*, a* and b* of crust decayed exponentially with time, whereas ΔE increased.

## 6.7 CONCLUSIONS

Physical properties of food products change during frying significantly. Shrinkage increases with frying time in the early stages of frying and decreases afterward or plateaus. The crust thickness increases nonlinearly with decrease in moisture content during frying. Apparent density reduces during frying due to water loss and oil gain while porosity increases. True density increases with moisture loss, but decreases with oil uptake. Increase in sample thickness increases the apparent density, but decreases porosity.

Generally the decrease in specific heat and thermal conductivity during frying is due to the decrease in moisture content and increase in oil content. Specific heat also decreases by increase in oil heat capacity due to oil degradation. All thermal properties decrease with increase in frying oil temperature.

The convective heat transfer coefficient increases with oil temperature and decreases with oil degradation. Heat transfer coefficient values at the top surface of a product are higher than those at the bottom surface due to higher agitation at the top created by bubbling. The heat transfer coefficient during frying is affected by bubble flow direction, velocity, bubble frequency and the magnitude of oil degradation. Oil temperature, frying time and location have significant effects on heat transfer coefficient.

Changes in pore structure influence moisture diffusivity and oil uptake. Moisture diffusivity is generally higher in foods having higher porosity due to an increase in moisture mobility. Moisture diffusivity increases with frying time and temperature, and is dependent mainly on product moisture content.

Potato maximum stress and corresponding strain increase during frying and with a decrease in frying temperature. Potatoes lose elasticity during frying. The texture of fried products is influenced by the type of the oil used and frying temperature and time. Desired color and flavor of fried products are achieved during frying as a result of the Maillard reaction. Redness (a*) increases as frying time and temperature increases. Decrease in sample thickness provides higher "a*" values.

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# 7 Acrylamide Formation During Frying

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## CONTENTS



## 7.1 INTRODUCTION

In April 2002, the Swedish National Food Administration (NFA), together with the University of Stockholm, reported on the finding of acrylamide in several baked, fried or deep-fat fried foods (National Food Administration Sweden 2002). The basis for this report was a presentation of appropriate research results (Tareke et al. 2000; Tareke et al. 2002). No message has changed the processing of fried products more than this communication. The report caused a lot of excitement in the media, among consumers and last, but not the least, in food safety authorities. During this period the media, but also some researchers, without strong data, speculated that $\leq 30\%$ of human cancer cases could be based on the intake of acrylamide in food. As a result of this commotion, a lot of research was undertaken to minimize the formation of acrylamide during the production of fried food, and industry started to transfer scientific results into the production process.

This chapter describes the path from the discovery of acrylamide in certain foods to the development of methods to avoid the formation of acrylamide during processing. This contribution depicts the mechanism and conditions for the formation of acrylamide in food. The most important question for the consumer (but also for the producer) is how to avoid acrylamide during production. To answer this question, this chapter gives a lot of information to reduce acrylamide formation. Processing parameters are very important, but also the raw material and frying equipment have a strong influence on acrylamide content in the product.

## 7.2 WHAT IS ACRYLAMIDE?

Until April 2002, acrylamide ($CH_2{=}CHCONH_2$, CAS registry number 79-0601) was known only as a chemical intermediate used since the mid-1950s for the preparation of polyacrylamide. The latter is applied for technical applications such as: effluent and sludge treatment; flocculates and coagulants; viscosity modifiers in crude oil recovery processes; binders in the paper industry; paints and coatings; toiletries and cosmetics; textile processing; and in the production of adhesives, tapes and gels, including electrophoresis gels. The first indication that acrylamide is also formed as a result of heating of biological material was that it is also a component of tobacco smoke (Bergmark 1997; European Commission 2000).

The monomer occurs in a white flowing crystalline form and is soluble in water, different alcohols, dimethyl ether and acetone; but it is insoluble in heptane and benzene. The solubility of acrylamide in water is one reason for its rapid distribution in the body after intake.

Research on acrylamide in food was very important because the compound was known to be mutagenic and carcinogenic in animals (Friedman, Dulak, and Stedham 1995; Johnson et al. 1986). This led to the classification of acrylamide as a probable human carcinogen by the International Agency for Research on Cancer (IARC) (International Agency for Research on Cancer 1994). A neurotoxic effect of acrylamide is subsequently described, particularly in studies with workers exposed to acrylamide via inhaled air and through the skin. Animal studies revealed an effect on the reproductive system, but a similar effect in humans has not been confirmed.

Studies about acrylamide in foods were based on studies of the University of Stockholm together with workers from Chinese factories that produced monomeric acrylamide and polyacrylamide (Calleman et al. 1994). These studies dealt with specific hemoglobin adducts of acrylamide found in the blood of (Bergmark 1997; Törnqvist 1994; Törnqvist et al. 1986) workers using acrylamide. Additional to the expected high level of adducts from acrylamide in the blood of tobacco smokers, Bergmark (1997) also found a high background adduct level in non-smokers which could not be explained. These results were subsequently confirmed after problems during the construction of a railway tunnel through the mountain ridge in Hallandsas. Vast amounts of acrylamide used for sealing the tunnel walls came into Vadbäcken, a rivulet close to one entrance of the tunnel construction. High levels of acrylamide adducts were found in poisoned cattle and fish who drank the water or lived in the rivulet. The exposure situation of the tunnel workers was clarified by investigation of hemoglobin adducts in the blood. Additionally, the situation of other people living inside and outside the contaminated area was studied. The results showed that people with no known exposure to acrylamide had inexplicably high background levels of hemoglobin adduct. Pharmacokinetic data from Calleman (1996) led to the assumption that a daily intake of about 100 mg of acrylamide would be necessary to reach the high background level in humans not exposed to acrylamide, as measured during the investigations (Törnqvist et al. 1998). It was also interesting that only low background levels of acrylamide adduct were found in animals. Tareke et al. (2000) showed the connection between increases of the level of acrylamide adducts in blood and the acrylamide content of food when they fed fried food to rats. This resulted in significantly higher levels of the hemoglobin adducts compared with those rats fed

a control diet (Tareke et al. 2000). Further analysis of different foods heated under controlled laboratory conditions led to the announcement of the Swedish National Food Administration and the University of Stockholm in April 2002 (Tareke et al. 2002).

## 7.3 FORMATION OF ACRYLAMIDE

Shortly after the first announcement about acrylamide in food, scientists from different countries identified possible pathways for the formation of acrylamide (Becalski et al. 2003; Mottram, Wedzicha, and Dodson 2002; Stadler et al. 2002a; Weißhaar and Gutsche 2002; Zyzak et al. 2003). The aim was to develop strategies to prevent or reduce the formation of this compound in foods.

Indications for the conditions necessary for the development and the main pathway for acrylamide formation gave the appearance of acrylamide in certain foods. The compound was found mainly in fried, deep-fat fried, roasted or oven-cooked foods on the basis of carbohydrates. Only traces of acrylamide were found in boiled or braised foods, indicating that significant formation of acrylamide during processing requires temperatures of $\geq$120°C. Therefore, it became clear that the conditions of the Maillard reaction, responsible for the development of a pleasant flavor of food during processing, also leads to the formation of acrylamide in heated foods.

From model experiments showing that the amount of acrylamide increased drastically if asparagine was heated in glucose or fructose, Weißhaar and Gutsche (2002) concluded that the major reactants are reducing sugars, and that the amino acid asparagine is the backbone of the acrylamide molecule. Both reactants form acrylamide at high temperature and low water availability. The importance of asparagine for the formation of acrylamide was confirmed by the fact that potato products are high in asparagine, with the highest amount related to the free amino acids in potatoes (93.9 mg/100 g) (Martin and Ames 2001).

Two hypotheses for the formation of acrylamide from asparagine were published. Mottram, Wedzicha, and Dodson (2002) suggested that the Strecker degradation of asparagine or methionine in the presence of $\alpha$-dicarbonyls is responsible for the formation of acrylamide. The reason for this suggestion was that significant amounts of acrylamide were formed when 2,3-butandione and asparagine were reacted in aqueous solution at high temperatures. For the formation of acrylamide according to this pathway, a reduction of the intermediate 3-oxopropionamide into 3-hydroxypropionamide, the Strecker alcohol of asparagine followed by a $\beta$-elimination of water, is necessary. Stadler et al. (2004) showed that the N-glycosyl of asparagine generated about 2.4 mmol/mol acrylamide, compared with 0.1–0.2 mmol/mol obtained with $\alpha$-dicarbonyls and the Amadori compound of asparagine. Additionally, they found that 3-hydroxypropanamide generated only low amounts of acrylamide ($\sim$0.23 mmol/mol), showing that this compound was not very effective as an acrylamide precursor, whereas hydroxyacetone increased the acrylamide yields to $>$4 mmol/mol. This indicates that $\alpha$-hydroxy carbonyls are much more efficient than $\alpha$-dicarbonyls in converting asparagine into acrylamide, and that the Strecker degradation seems to have only limited importance on the formation of acrylamide.

Stadler et al. (2002a) assumed that glycoconjugates such as N-glycosides and related compounds formed from asparagine (Schiff bases when viewed in their open-chain tautomeric form) are key intermediates for the formation of acrylamide. Only minor amounts of acrylamide resulting from the reaction of N-glycosides formed from glutamine and methionine were found. The importance of asparagine for the formation of acrylamide was confirmed by Becalski et al. (2003), who also found asparagine to be the main precursor of acrylamide in model reactions between amino acids and glucose. In 2003, Zyzak et al. (2003) investigated the mechanism for the formation of acrylamide using a model fried potato snack system. They also found the contribution of a Schiff base as intermediate for the formation of acrylamide, followed by decarboxylation and elimination of ammonia or a substituted imine. Yaylayan, Wnorowski, and Perez Locas (2003) also confirmed this hypothesis by showing the importance of the Schiff base of asparagine, which corresponds to the dehydrated N-glucosyl compound (Figure 7.1).

### 7.3.1 The Role of Lipids on the Formation of Acrylamide

The reaction of asparagine with reducing sugars is accepted as the main pathway for the formation of acrylamide in food, but nevertheless other pathways or precursors are in the discussion. Directly after the first announcement of acrylamide in foods, acrolein became a suspect because its molecular structure is similar to acrylamide and it is formed at higher temperatures during the frying process. Gertz and Klostermann (2002) suggested that monoacylglycerols may decompose during frying to fatty acid and acrolein, followed by a cyclic mechanism resulting in the formation of acrylamide after oxidation in the presence of ammonia. The mechanism for the formation of free fatty acids from monoacylglycerols is known as "ester pyrolysis" and is different from the formation of short-chain fatty acids formed during the oxidation of polyunsaturated fatty acids. Gertz and Klostermann (2002) also found significantly higher amounts of acrylamide in French fries fried in palm olein than that in French fries fried in sunflower or rapeseed oil. They supposed that the comparably high amount of diacylglycerols (about 8%) and monoacylglycerols (0.3–0.5%) in palm oil products compared with other edible oils could be responsible for the different acrylamide formation by emulsification of the components.

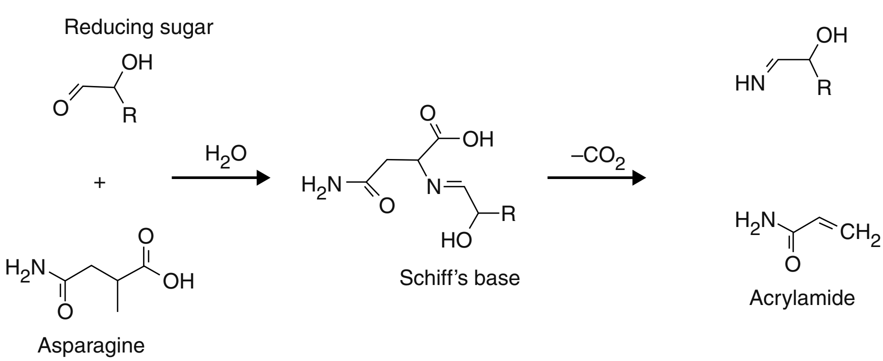



**FIGURE 7.1** Proposed mechanism of acrylamide formation.

Ehling, Hengel, and Shibamoto (2005) also found a strong influence of the oil type on acrylamide formation in model systems consisting of pure amino acids and oil at elevated temperatures with the following decreasing order with asparagine as amino acid: sardine oil (642 μg acrylamide/g asparagine) > cod liver oil (435.4 μg/g) > soybean oil (135 μg/g) > corn oil (80.7 μg/g) > olive oil (73.6 μg/g) > canola oil (70.6 μg/g) > corn oil (stripped) (62.1 μg/g) > beef fat (59.3 μg/g) > lard (36.0 μg/g). From this result, they concluded that three-carbon units such as acrolein or acrylic acid, which are formed as degradation products of lipids during heating, can form acrylamide in the presence of amino acids, especially asparagine, but without the need for reducing sugars (Figure 7.2).

In contrast with these results, Matthäus, Haase, and Vosmann (2004) found no significant difference in the acrylamide concentration of French fries fried in different edible oils. Acrylamide formation in French fries fried in vegetable fats was slightly higher than in French fries fried using vegetable oils, but these differences were not significant ($P < 0.05$) (Figure 7.3). There was no effect of the oil quality, characterized by the amount of oligomer triglycerides on the acrylamide concentration in French fries. Despite progressive aging of the oil during frying, no increase of acrylamide was noticeable. They concluded that the application of used frying oil did not result in higher amounts of acrylamide in French fries in comparison with fresh oil. Williams (2005) also found no significant effect of the oil type ($P = 0.364$) on acrylamide formation. He concluded that the composition of the oil did not influence the formation of acrylamide. Williams (2005) did not detect any correlation between oil condition and acrylamide formation.

The same result was found by Mestdagh, de Meulenaer, and van Peteghem (2007) who investigated the influence of used frying oils using a closed stainless steel tubular reactor. They observed no significant influence of used oil on acrylamide formation as a result of oil oxidation. From this result, they concluded that oil oxidation may affect heat transfer between oil and product, but these changes were not sufficient to significantly alter acrylamide formation in the product. Mestdagh, de Meulenaer, and van Peteghem (2007) found that none of the oil hydrolysis products

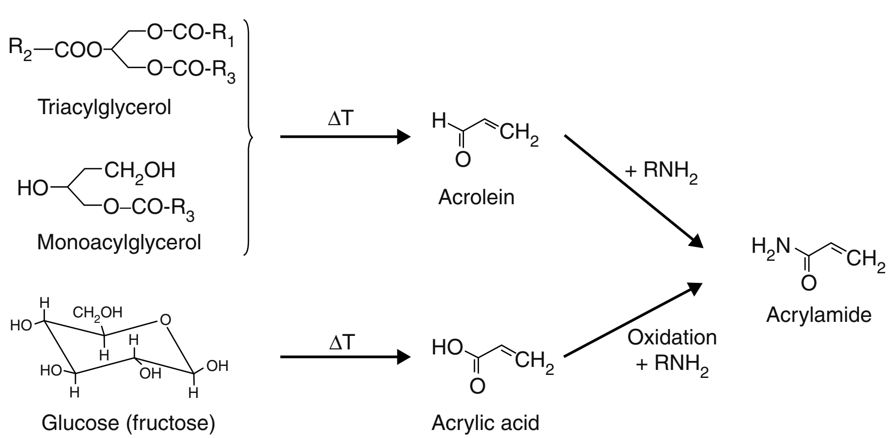



**FIGURE 7.2** Alternative pathways for acrylamide formation.

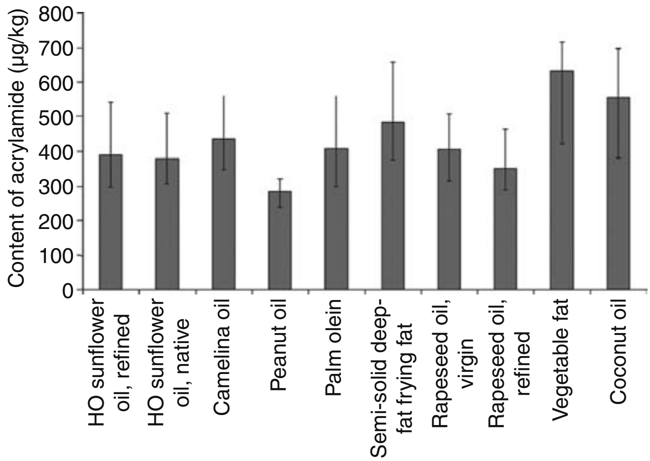



**FIGURE 7.3** Influence of oil type on acrylamide formation (From Matthäus, B., Haase, N. U., and Vosmann, K., *European Journal of Lipid Science and Technology,* 106. Factors affecting the concentration of acrylamide during deep-fat frying of potatoes, 793–801, copyright (2004) Wiley-VCH Verlag GmbH & Co. KGaA. With permission).

was a relevant precursor for the formation of acrylamide under normal heating conditions, although glycerol was suspected to be a precursor for the development of acrylamide by Gertz and Klostermann (2002).

In another work based on the use of a heating system consisting of a closed stainless steel tubular reactor, Mestdagh et al. (2005) found a general effect of the oil on acrylamide generation. Artificial mixtures without oil produced less acrylamide than mixtures containing certain amounts of oil.

Gertz and Klostermann (2002) assumed that the usage of dimethylpolysiloxane (DMPS) (silicone oil, E900) in frying oils may cause the formation of higher amounts of acrylamide. DMPS is permitted as an antifoaming agent for use in frying fats and oils according to Directive 95/2/EG (Anonymous 1995). This agent is commonly used in amounts between 1 mg/kg and 2 mg/kg fat or oil to prevent undesirable formation of foam during frying. Foam formation could result in endangering of staff, but also in a higher intake of oxygen into the frying medium, by which the stability of the oil would decrease. Silicon oil has an effect by edging out foam-forming substances from the interface between the liquid and gaseous phase by formation of a whole interfacial film or by increasing the interfacial tension of water. As a result of an interfacial film consisting of DMPS removal of acrolein or acrylamide by evaporation of water, steam may be hindered or reduced, leading to higher concentrations of acrylamide in the product (Gertz and Klostermann 2002). This assumption was confirmed by the authors when they found higher acrylamide levels in fried products after use of silicone in comparison with silicone-free fats and oils (Gertz and Klostermann 2002). In contrast, other authors (Kreyenmeyer 2003; Matthäus, Haase, and Vosmann 2004; Mestdagh, de Meulenaer, and van Peteghem 2007) showed no significant increase of acrylamide levels after use of silicone oil, and also the concentration of silicone in the oil or fat had no effect (Matthäus, Haase, and Vosmann 2004) (Figure 7.4).

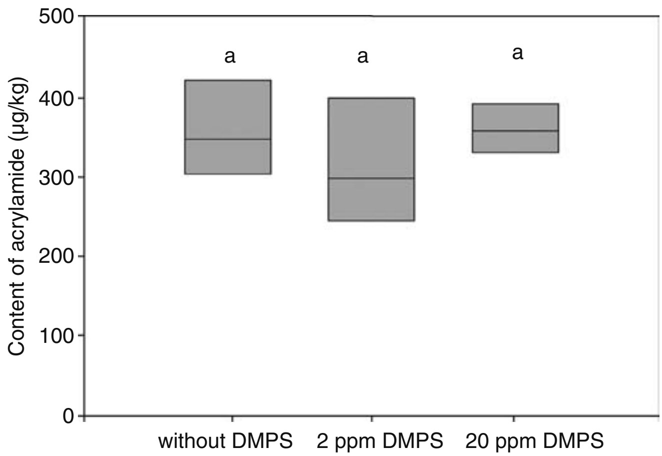



**FIGURE 7.4** Influence of dimethylpolysiloxane (DMPS) on acrylamide formation (different characters above the columns show significantly different results).

Totani et al. (2007) investigated used frying oils from food manufacturing companies for the content of acrylamide. Acrylamide was not found in a detectable amount (detection limit 0.02 mg/kg) in any of the used frying oils. The results negate the finding of Becalski et al. (2003), i.e., acrylamide was formed from oils and ammonia derived from the degradation of nitrogen-containing compounds present in foods.

Acrylic acid can also be generated from aspartic acid by the Maillard reaction, in analogy to the formation of acrylamide from asparagine (Stadler et al. 2002b). In the following reaction, ammonia produced from amino acids via Strecker degradation can react with acrylic acid to form acrylamide (Yasuhara et al. 2003). The reaction is strongly limited by the availability of free ammonia in the food matrix and by the extreme volatility of ammonia at temperatures necessary for the formation of acrylamide (Yaylayan et al. 2005). Stadler et al. (2002b) showed that the reaction between aspartic acid and fructose produces acrylamide at levels 1000-fold below the levels measured for the reaction between asparagine and fructose.

### 7.3.2 Strategies to Reduce Acrylamide in Fried Food

The main problem in developing strategies for prevention of acrylamide formation in food is that the main pathway is the same as for the formation of compounds with pleasant and desirable aromas during food preparation. Difficulties arise because on one hand exists the legitimate expectation of the consumer for high-quality products, and on the other hand the amount of acrylamide in food should be minimized. Although it seems possible to produce food with a very low acrylamide concentration, the consumer will most probably reject these products if the quality is poor. Therefore, the aim of prevention strategies has to be to reduce the acrylamide concentration in food while maintaining the quality of the product.

With this objective, a lot of research was carried out since the first announcement of the finding of acrylamide in food. Most studies were done in the field of deep frying because high amounts of acrylamide were found especially in deep-fat fried potatoes, French fries or Potato crisps (Figure 7.5). According to the 64th meeting of the Joint FAO/WHO Expert Committee on Food Additives, the intake estimates were 0.3–2.0 μg/kg body weight per day for the average person in the general population, whereas the intake for high percentiles consumers (90th to 97.5th) come to 0.6–3.5 μg/kg body weight per day, with $\leq$ 5.1 μg/kg body weight per day for the 99th percentile consumer (Anonymous 2005). Expressed on the basis of body weight, the intake of acrylamide by food is about 2–3 times higher for children in comparison with adult consumers.

Researchers all over the world started to search for the solutions to reduce the amount of acrylamide in the products without changing the quality because potato crisps and French fries are widely consumed by the population of most countries (Figure 7.6) (Amrein et al. 2003; Biedermann and Grob 2003; Biedermann et al. 2002a; Fiselier et al. 2006; Gertz and Klostermann 2002; Gertz, Klostermann, and Kochhar 2003; Matthäus, Haase, and Vosmann 2004; Pedreschi, Kaack, and Granby 2004; Totani et al. 2007).

The concentration of acrylamide in food is affected by different factors which are derived from the process, raw materials as well as from the equipment. Each of these factors contributes to the total concentration of acrylamide, whereas the individual contribution differs. Additionally, the individual factors affect each other during processing.

This complexity of the problem makes the objective of reducing acrylamide in the product with simultaneous maintenance of the product quality very difficult.

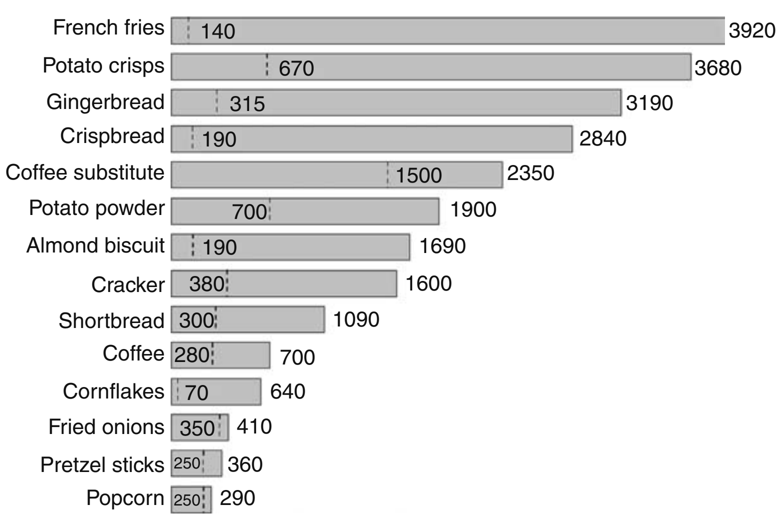



**FIGURE 7.5** Examples for acrylamide contents in different food (μg/kg) (bars: maximum value found in food; dotted lines: mean value found in this group of food).

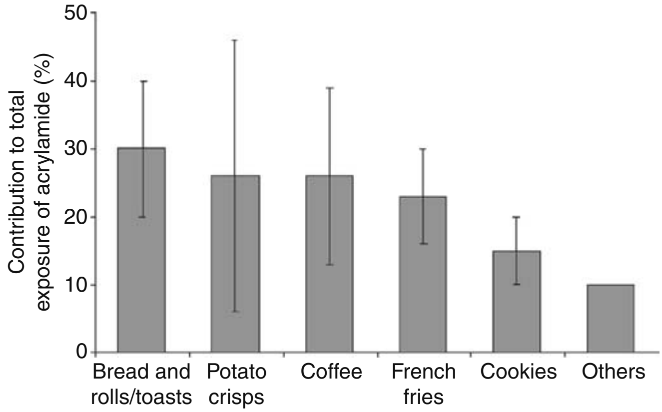



**FIGURE 7.6** Contribution of different food to the total exposure of humans with acrylamide.

#### 7.3.2.1 Process Parameters

Shortly after the first announcement of the finding of acrylamide in food, it became obvious that process conditions, especially temperature and time, have a strong influence on the formation of acrylamide (Gertz and Klostermann 2002; Gökmen, Palazoglu, and Senyuva 2006; Rydberg et al. 2003; Stadler et al. 2002a).

During frying, the heating medium often reaches 160–200°C, whereas the product being fried is cooled by water evaporation, resulting in temperatures in the product of <100°C. Despite this cooling effect of the vapours from the food, the temperature at the surface increases with frying time and leads to a browning of the product because of the Maillard reaction. From the inner part of the product to the surface, a temperature gradient can be found from <100°C to a temperature near the temperature of the frying medium at the surface.

Gertz and Klostermann (2002) compared the formation of acrylamide during frying at different temperatures. They concluded that it is strongly recommended that fryer operators should lower the frying temperature and use reliable control of temperature during frying. A further recommendation was to limit the temperature to 175°C. This result was confirmed by Matthäus, Haase, and Vosmann (2004), who investigated the effect of temperatures between 150°C and 190°C and frying times between 5 min and 10 min on acrylamide formation of French fries. It was obvious that the content of acrylamide increased not only with increasing temperature, but also with the time of frying. The amount of acrylamide was relatively low at temperatures between 150°C and 175°C, but there was a drastic increase when the temperature reached $\geq$ 180°C. The time-dependent increase of acrylamide at constant temperatures followed a linear function with enhanced slope at higher temperatures. The linear correlation between acrylamide content and frying time ranged between $r = 0.9072$ for 150°C and $r = 0.9956$ for 190°C (Figure 7.7). On the other hand, looking at the temperature at constant frying time, the increase of the acrylamide concentration in the product followed an exponential function for longer frying times, with a stronger increase of acrylamide concentration at

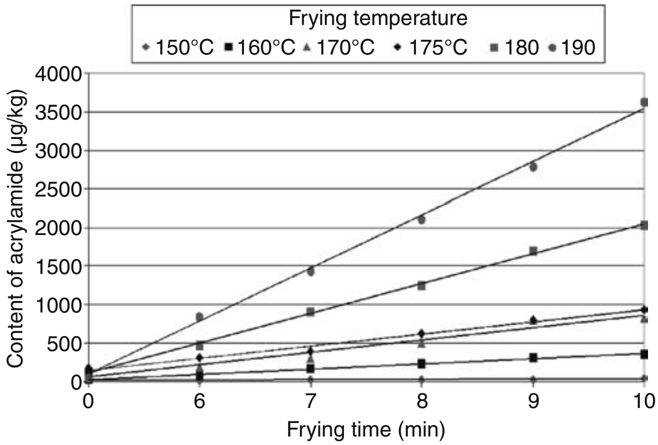



**FIGURE 7.7** Influence of frying time on formation of acrylamide in French fries.

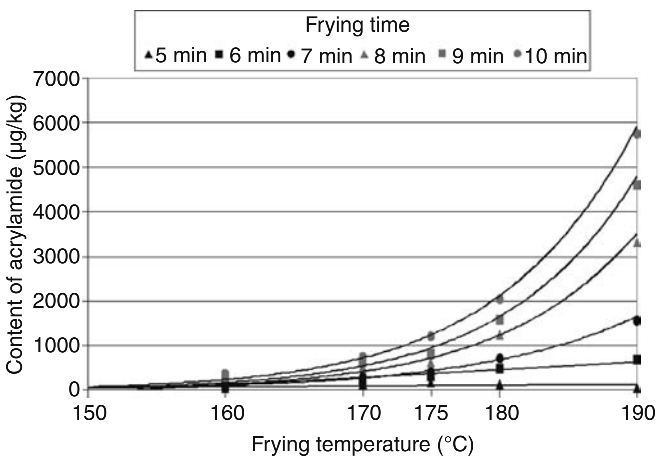



**FIGURE 7.8** Influence of frying temperature on the acrylamide content of French fries.

temperatures >170°C (Figure 7.8). The shorter the frying time, the smaller is the acrylamide formation, even at higher temperatures. It was concluded that temperature reduction with simultaneous lengthening of the frying time will result in an absolute reduction of the acrylamide concentration in the product (Matthäus, Haase, and Vosmann 2004).

The same result was found by Gökmen, Palazoglu, and Senyuva (2006) for temperatures of 150°C, 170°C and 190°C. They observed an exponential increase in acrylamide content with increasing temperature for a constant frying time, but they emphasized that this relationship was true only for a frying time of 9 min, not for shorter processing times. Williams (2005) found a highly significant influence ($P < 0.001$) of cooking temperature and time on acrylamide formation, reflecting that the extent of formation of acrylamide in heated foods was dependent on the severity and duration of heat exposure.

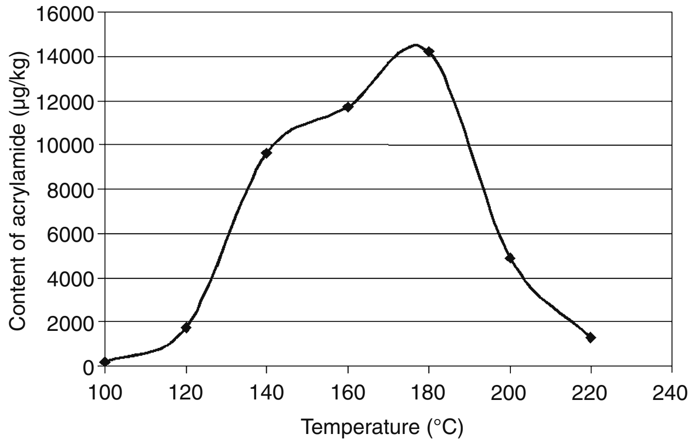



**FIGURE 7.9** Acrylamide formation in instant potato powder at different temperatures (From Weißhaar, R., *European Journal of Lipid Science and Technology,* 106. Acrylamide in heated potato products - analytics and formation routes, 786–792, copyright (2004) Wiley-VCH Verlag GmbH & Co. KGaA. With permission).

Temperatures of >180°C resulted in degradation of acrylamide and led to lower amount of acrylamide in products (Figure 7.9) (Mottram, Wedzicha, and Dodson 2002; Weißhaar 2004). From this result, it can be assumed that acrylamide formation represents a balance of competing complex processes of formation and destruction (Anonymous 2005).

During frying, acrylamide formation takes place mainly at the surface of the product because of the high temperature and low moisture content in the outer zones of the raw material. This results in a steady improvement of the conditions for the Maillard reaction, which favors the formation of acrylamide and consequently leads to high amounts of acrylamide in the surface while the concentration of acrylamide in the core remains relatively low. Acrylamide concentration is negatively correlated with moisture content (Matthäus, Haase, and Vosmann 2004) (Figure 7.10).

Matthäus, Haase, and Vosmann (2004) showed that with increasing temperature, but also with increasing frying time, the final moisture content in French fries decreased. While frying at 150°C resulted in an acceptable moisture content, with increasing temperature it became increasingly difficult to reach the optimal moisture content of French fries (38–45%) and, as a consequence, the optimal quality of ready-to-eat French fries. The authors also showed that with decreasing moisture content in the product, the content of acrylamide increased drastically.

Gökmen, Palazoglu, and Senyuva (2006) showed that evaporation is an important barrier to internal energy increase and consequently to acrylamide formation. They monitored the temperature of the surface and the core of potato strips during frying at different oil temperatures and the acrylamide contents of resulting products. The results confirmed that acrylamide was formed mainly at the surface, where concentrations of 72 µg/kg, 2747 µg/kg and 6476 µg/kg were found after frying for 9 min at 150°C, 170°C and 190°C, respectively, whereas the amounts in the core were only 376 µg/kg after frying at 190°C. The authors concluded that with

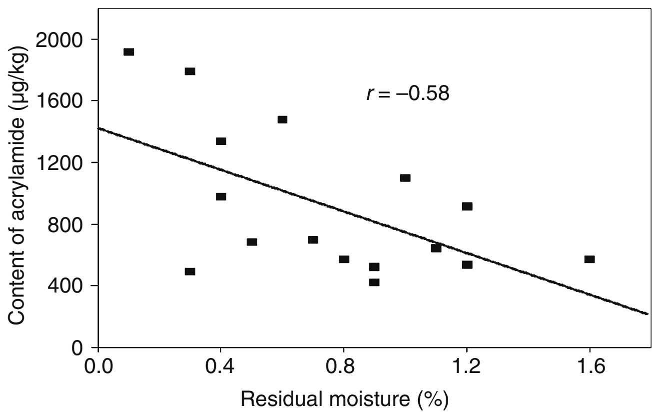



**FIGURE 7.10** Correlation between residual moisture in the product and acrylamide content.

increasing oil temperature, the greater energy input resulted in faster drying of the product at the surface and therefore the better conditions for acrylamide formation were reached sooner.

Amrein et al. (2006) investigated the effect of moisture contents on acrylamide formation and browning and its influence on the activation energy of the browning reaction and acrylamide formation. They found that browning rates, determined as relative brightness (L value), increase with decrease of the moisture contents in the products. Linear correlation was found between acrylamide content in heated potato powder and "L" value as well as "a" value if samples with the same moisture contents were compared. This result was also found for fried potato slices (Pedreschi et al. 2005) and potato strips (Pedreschi, Kaack, and Granby 2006). Looking at the activation energy necessary for acrylamide formation and browning, Amrein et al. (2006) found differences in the influence of the moisture content of the product on browning and acrylamide formation. At low moisture contents up to 20 g/100 g, the activation energy for acrylamide formation was higher compared with the one for browning, while no large differences were found for moisture contents >20 g/100 g. With respect to acrylamide formation, Amrein et al. (2006) found that the activation energy at low moisture content (<20 g/100 g) was 80–120 KJ/mol, which was about 80% higher than that for browning. As a result, it was concluded that acrylamide formation becomes particularly temperature-dependent at low moisture contents. Toward the end of the frying process, moisture content reduces to a low level and temperature becomes a very critical parameter for the formation of acrylamide. Because the activation energy for the formation of acrylamide was higher than for browning, a lower temperature toward the end of the frying process was recommended to reduce the content of acrylamide in the product while maintaining the product quality (e.g., color).

During the frying process, oil temperature drops drastically on adding the raw potato and the initial temperature is reached again (if at all) only at the end of the frying process. The temperature during this period of the process is the most important because acrylamide formation takes place mainly at the end of the frying

process when moisture content of the material reaches a critical amount. Using an initial temperature of 170–175°C with a drop to 140–145°C and virtually isothermal frying at 160°C resulted in products of similar quality and lower acrylamide concentration, while at initial temperatures of <170°C the quality of French fries with regard to crispness and flavor was negatively affected (Fiselier et al. 2006). An increase of the virtually isothermal frying temperature for about 10°C resulted in doubling of the acrylamide level in the product. From this result, Fiselier et al. (2006) recommended that optimized fryers should program temperature, allowing an initial temperature drop, but ensuring efficient heating to prevent a temperature drop below a given limit. The initial temperature must be restored after the end of the frying process before frying the next portion.

Several investigations confirmed that a lower frying temperature at the end of the process resulted in a reduction of the acrylamide level in the product (Fiselier et al. 2006; Granda, Moreira, and Tichy 2004; Grob et al. 2003; Matthäus, Haase, and Vosmann 2004).

Taubert et al. (2004) showed that the variation of acrylamide contents in the products at a given degree of surface browning strongly depended on the surface-to-volume-ratio (SVR). The acrylamide level in slices of 15 mm varied between 1000 μg/kg and 1500 μg/kg, while it was between 2500 μg/kg and 13000 μg/kg in slices of 3 mm. Taubert et al. (2004) assumed that the heat transfer to the core may take longer in products with low SVR. They found a linear correlation between browning level and acrylamide content for the samples having small surface area ($r^2 = 0.74$, $P < 0.001$), while the correlation became insignificant with increasing surface area of the products. Lack of correlation between surface browning and acrylamide content in material with high SVR was explained with the net degradation of acrylamide at long processing times, which did not occur with a decrease of browning.

In general, the SVR of the product seems to be a very important point for acrylamide generation. Taubert et al. (2004) found a constant increase of acrylamide formation with increasing temperature only in potato pieces with low SVR (0.27 $mm^{-1}$). In samples with higher SVR (0.80 $mm^{-1}$ and 2.12 $mm^{-1}$) an absolute maximum of acrylamide levels was reached at 160°C and 180°C, respectively. The investigation also showed a decrease of acrylamide levels at high temperatures and long processing times when samples with high SVR were used.

Matthäus, Haase, and Vosmann (2004) also observed that par-fried coarse-cut potato stripes (14 × 14 mm; SVR: 3.3 $cm^{-1}$) showed significantly ($P < 0.05$) lower amounts of acrylamide than fine-cut stripes (8 × 8 mm; SVR: 5.4 $cm^{-1}$) using a constant frying time within the experiment. The sensory quality of deep-fat fried products of both sizes was of good and comparable quality at the conditions used for frying. The authors explained this finding by saying that during the process of deep-fat frying, water is removed from the surface of the product, resulting in the improvement of the conditions for acrylamide formation. Therefore, if the surface area of the product increases in comparison to its weight, the formation of acrylamide is favored and this resulted in a faster dehydration of smaller potato stripes and higher amounts of acrylamide in comparison with potato stripes with lower SVR. The effect of size on acrylamide content of potato slices can be seen in Figure 7.11.

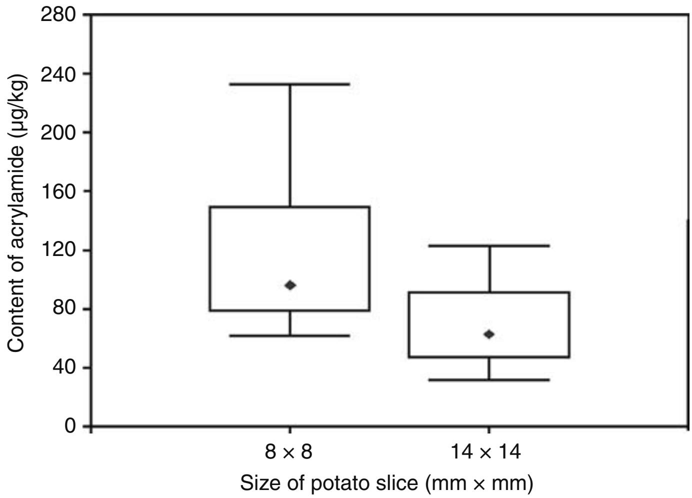



**FIGURE 7.11** Influence of the geometry (size) of French fries (two varieties) on the acrylamide level (From Matthäus, B., Haase, N. U., and Vosmann, K., *European Journal of Lipid Science and Technology,* 106. Factors affecting the concentration of acrylamide during deep-fat frying of potatoes, 793–801, copyright (2004) Wiley-VCH Verlag GmbH & Co. KGaA. With permission).

### 7.3.2.2 Raw Material

Another important factor for the formation of acrylamide is the concentration of amino acids and reducing sugars within the raw material used for the preparation of food. Different researchers (Amrein et al. 2003; Biedermann et al. 2002b; de Wilde et al. 2005; Matthäus, Haase, and Vosmann 2004; Williams 2005) showed a significant correlation between glucose content of potatoes and acrylamide formation in the fried products, while no correlation existed between the content of free asparagine and acrylamide content (Figure 7.12). This indicated that the amount of reducing sugars in the raw material is decisive for the formation of acrylamide and the limiting factor in generation of acrylamide; whereas changes in asparagine concentration did not influence acrylamide level. The explanation for this finding is that the concentration of asparagine is several times higher than the concentration of reducing sugars. Thus, asparagine is available for the formation of acrylamide in excess, resulting in a stronger dependence of acrylamide formation from the concentration of reducing sugars. This statement is supported by the finding of Whitfield (1992) that reducing sugars determine browning and flavor formation by the Maillard reaction.

Because potatoes are vegetative organs of the plant, their composition strongly depends on the dominating environmental conditions such as nutrient supply and water availability at the point of harvest (Burton 1989; Hippe 1988; Pawelzik and Delgado 1999), but genotype, location of cultivation, and storage conditions also have an influence on composition (Amrein et al. 2003; Davies 1977; Haase and Weber 2003).

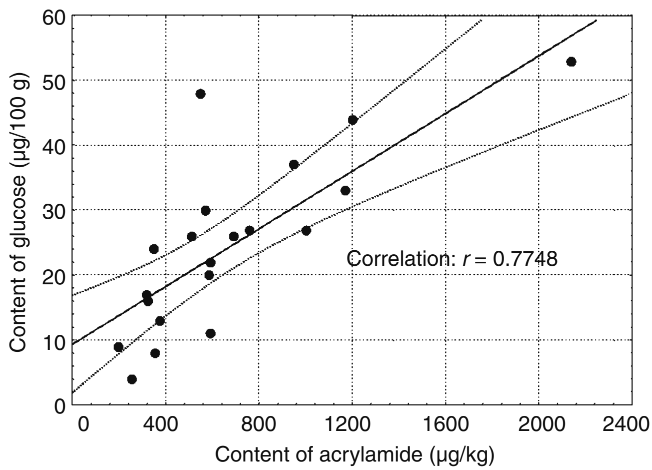



**FIGURE 7.12** Correlation between glucose content in potatoes and acrylamide content in the fried product.

Thus, one way to reduce the content of acrylamide in the product is to reduce the content of the reactants directly in the raw material by breeding new varieties, changing the conditions of cultivation or the storage conditions, or appropriate pretreatment of the raw material before processing.

The first alternative is very costly because breeding new varieties low in asparagine and reducing sugar contents is time-consuming and a successful conclusion is not guaranteed because a lot of other factors are also responsible for the composition. Nevertheless, different researchers have shown the great variability in different cultivars of potatoes (Amrein et al. 2003; Biedermann et al. 2002b; Haase et al. 2003a), indicating the great potential of breeding to reduce the potential of acrylamide formation. Haase et al. (2003a) found that the potato variety Tomensa showed only a slight increase of acrylamide formation with frying temperature, whereas the increase was much more marked for potato crisps produced from the variety Saturna. Amrein et al. (2003) analyzed glucose, fructose, sucrose, free asparagine and free glutamine of 74 samples of potatoes from 17 cultivars and found a great variation of the content of asparagine (0.201–0.425%) and glucose (0.0335–0.255%), resulting in a different acrylamide formation potential. Similar results with regard to differences in the composition of different varieties were found by Williams (2005) (asparagine: 0.139–2.113%; glucose: 0.399–8.699%) and Becalski et al. (2004) (asparagine: 0.149–1.137%; glucose: 0.007–0.628%). The field site determines the environmental conditions and also has a significant influence on the concentration of the reactants and consequently on the potential of acrylamide formation in the potatoes (Amrein et al. 2003; Haase et al. 2003a; Haase et al. 2003b). The effect of potato varieties on acrylamide content is given in Figure 7.13.

The glucose content of the raw material strongly influences the browning of the product. Granda, Moreira, and Castell-Perez (2005) showed that with increasing amounts of glucose in a model system of infused leached potato slices, the "L"

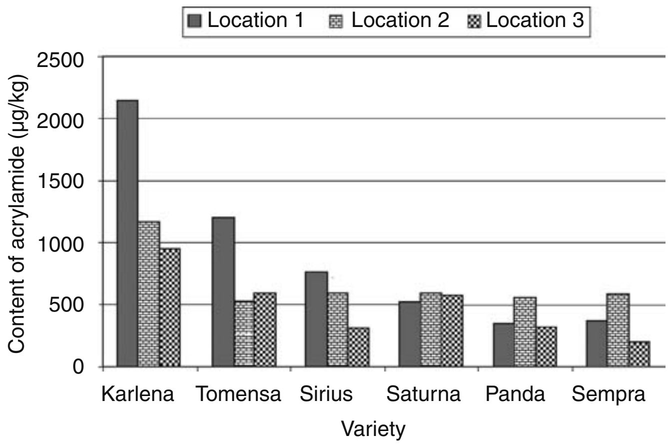



**FIGURE 7.13** Influences of the variety of potatoes on the potential of acrylamide formation.

value decreased, i.e., the potatoes became darker, while no effect was found for the increase of asparagine. For the color values "a" and "b", they also found an increase with increasing amounts of glucose, but no effect of asparagine was found. Granda, Moreira, and Castell-Perez (2005) obtained a linear correlation between "a" value and acrylamide concentration at constant asparagine levels, and an exponential correlation between "b" value and acrylamide concentration. They subsequently showed that at constant "a" and "b" values, the acrylamide amount in the product increased with increasing concentration of asparagine, indicating that the concentration of acrylamide in two chips with a similar color can be completely different with respect to the amount of asparagine.

A further important possibility to influence the potential of acrylamide in potatoes during deep-fat frying is the storage temperature of the potato tubers before processing. During post-harvest storage, potato tubers are enriched in low molecular weight carbohydrates (Haase and Weber 2003; Richardson, Davies, and Ross 1990), which results in sweetening of the potatoes. This effect is accelerated during storage of potato tubers at low temperatures, which leads to remarkably higher concentrations of glucose and fructose. As a result of these higher levels of reducing sugars, the potential of acrylamide formation increases drastically. Biedermann et al. (2002a), Matthäus, Haase, and Vosmann (2004) and Noti et al. (2003) showed that potatoes stored at 4°C had significantly higher potential for acrylamide formation, while the acrylamide levels remained lower in potatoes stored at 8°C (Figure 7.14). Another result was that differences between field sites were low at a storage temperature of 8°C, while a lower storage temperature resulted in a more marked differentiation of the single growing site in the potential for acrylamide formation.

High storage temperatures of potatoes require the application of anti-sprouting chemicals. de Wilde et al. (2005) investigated the effect of sprout inhibitors and reconditioning of potatoes after storage at lower temperatures on the formation of acrylamide. By reconditioning potatoes for 3 weeks at 15°C, the reversible nature of the formation of low molecular weight sugars during storage at 4°C can be pushed

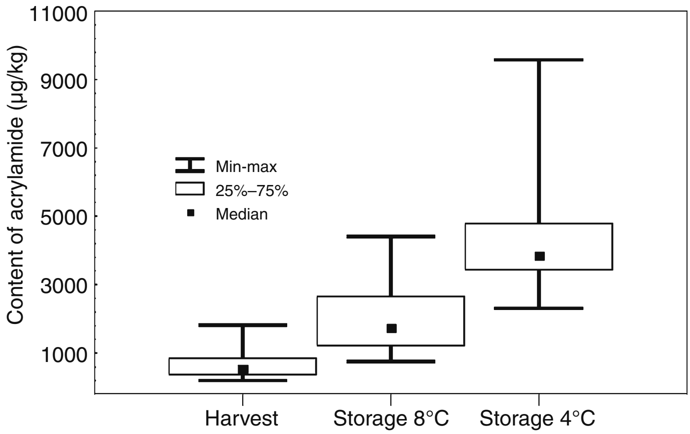



**FIGURE 7.14** Influence of the storage conditions on the formation of acrylamide.

back, resulting in a significant reduction of reducing sugars. After storage of potatoes for 8 weeks at 4°C, reconditioning had no significant effect on acrylamide level but, after longer storage at low temperature (16 and 24 weeks, respectively) reconditioning for 3 weeks caused a significant and drastic reduction of the acrylamide level in potatoes being fried. Chemical sprout suppressors are necessary because potatoes start to sprout during reconditioning. de Wilde et al. (2005) found no significant effect of chlorpropham, isopropyl-N-(3-chlorophenyl) carbamate (CIPC) treatment during reconditioning on the acrylamide level of potatoes after frying.

Another effective way to reduce the reactants of acrylamide formation in the raw material is appropriate pretreatment of potatoes before processing to remove asparagine and reducing sugars, but product quality must be kept in mind. The different possibilities to reduce the content of reactants comprise blanching and soaking, degradation of asparagine by the enzyme asparaginase, or using antioxidants.

Williams (2005) found no significant effect of soaking potatoes in water before frying on glucose and asparagine contents ($P = 0.180$). This was confirmed by Pedreschi et al. (2007a), who also observed that soaking of potato slices before frying resulted in no significant reduction of the glucose or asparagine content in the raw material. Kita et al. (2004) found only a decrease of the reactants by 10 and 24%, respectively, after soaking potato slices in pure water for 1 min and 60 min at 20°C. This effect was improved at 70°C, which resulted in a decrease of acrylamide formation by 19% and 26%, respectively, for 1 min and 3 min blanching in pure water. This result was consistent with Jung, Choi, and Ju (2003), who found a reduction of about 25% in acrylamide content of French fries resulting from dipping of potato strips in distilled water for 1 h. Pedreschi et al. (2007a) found that the content of acrylamide in the fried product decreased with increase of soaking time. In comparison with control, a reduction of the acrylamide content of about 15% after 60 min and of about 30% after 120 min of soaking was found.

Formation of acrylamide is subject to strong dependence on pH, resulting in a maximal acrylamide formation at about ≥pH7 and decreasing the amounts of acrylamide with decrease of the pH value of the product (Weißhaar and Gutsche

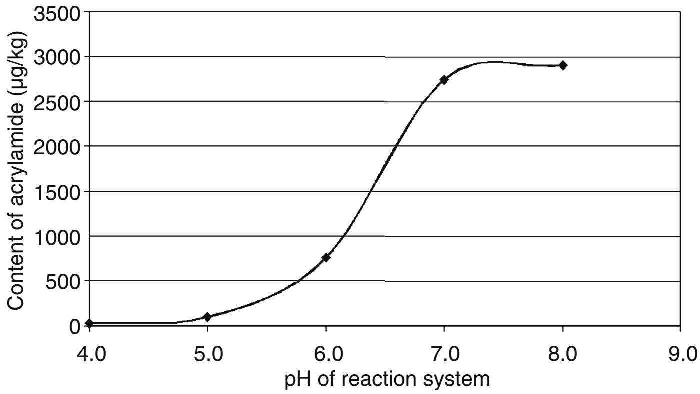



**FIGURE 7.15** Influence of pH value on acrylamide formation in a model system of asparagine and glucose (From Weißhaar, R., *European Journal of Lipid Science and Technology*, 106. Acrylamide in heated potato products – analytics and formation routes, 786–792, copyright (2004) Wiley-VCH Verlag GmbH & Co. KGaA. With permission).

2002; Rydberg et al. 2003) (Figure 7.15). Jung, Choi, and Ju (2003) supposed that the reaction of acrylamide formation is blocked by the conversion of free non-protonated amine into non-nucleophilic protonated amine by lowering the pH of the reaction system. From this, the idea arises to soak potato slices not only in water, but also in acidic solutions (Kita et al. 2004; Pedreschi et al. 2007a) with the aim to extract amino acids and sugars from the potatoes in combination with a decrease of pH of the raw material. Pedreschi et al. (2007a) found no significant difference in the glucose and asparagine content of the control sample and those soaked in citric acid and sodium pyrophosphate. With regard to the content of acrylamide in the fried product, soaking in citric acid was remarkably more effective than the use of sodium pyrophosphate. While soaking in the latter showed no significant difference from the control, the use of citric acid reduced the content of acrylamide by 86%, 47% and 28% at frying temperatures of 150°C, 170°C and 190°C, respectively. Kita et al. (2004) found the highest decrease (90%) of the acrylamide content after soaking potato slices in acetic acid solution (60 min/20°C). However, soaking potato slices in citric and acetic acid for 60 min resulted in a sour taste of the product. The authors also found a significant decrease of acrylamide content (74%) in potato crisps after soaking potato slices in 1% NaOH solution. Unfortunately, the base solution influenced the appearance as well as the taste and flavor of the crisps, which was not acceptable.

More effective than soaking is blanching of potatoes before frying. This method is used to improve the color and texture of potato crisps, and to reduce oil uptake by gelatinization of surface starch (Taubert et al. 2004). With regard to acrylamide, Haase et al. (2003a) found that blanching resulted in a reduction of about 60% in the acrylamide content of the fried product in comparison with a control without blanching depending on the raw material (potato variety and field site) and production conditions (blanching and frying temperature). The higher the frying temperature, the higher was the effect on reduction of acrylamide in the product (Figure 7.16). Similar results were found by Pedreschi, Kaack, and Granby (2004), who compared

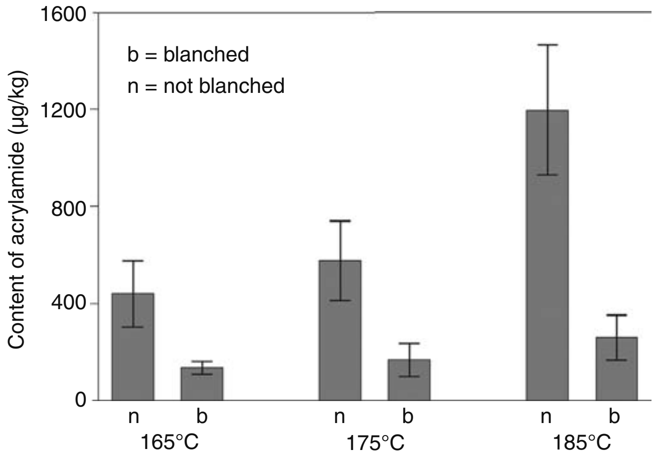



**FIGURE 7.16** Influence of blanching of potatoes and frying temperature on the acrylamide content of potato crisps.

the effect of blanching at different temperatures and times and found, on average, a reduction of the glucose and asparagine content by 76% and 68%, respectively, in comparison with non-blanched potatoes. May et al. (2006) found a reduction in the content of reducing sugars after hot-water blanching of raw potato chips between 51% and 62%. The extent of reduction followed an exponential function depending on blanching time. Kita et al. (2004) found a 50% decrease of the acrylamide content in potato crisps after only 3 min of blanching at 70°C in solutions of citric acid and acetic acid. One observed disadvantage was that a slight sour taste was detected in crisps blanched for 1 min or 3 min at 70°C in citric acid solution. No detectable taste differences were observed when acetic acid was used, indicating that acetic acid could be a better acidulant for the pretreatment for potato crisps.

A further possibility to reduce the content of acrylamide in the product is soaking potato slices in NaCl solution after blanching. The use of NaCl solutions prior to frying results in a significant reduction of oil absorption and an increased texture parameter in the product (Bunger, Moyano, and Rioseco 2003). Pedreschi et al. (2007b) showed that this procedure also dramatically reduced acrylamide formation in potato chips (about 90%) in comparison with control chips, with simultaneous improvement of the color.

Kim, Hwang, and Lee (2005) showed that addition of lysine, glycine and cysteine was suitable to reduce the concentration of acrylamide in aqueous model systems by 91%, 95%, and 87%, respectively. Using these amino acids in fried model snacks, the authors found an effect of lysine and glycine, depending on the concentration of amino acid and the frying time, but no influence of cysteine on acrylamide formation. The low solubility of cysteine in aqueous solution was probably responsible for this effect.

Similar effects were found by Rydberg et al. (2003), who describe a reduction of the acrylamide levels in homogenized potatoes heated at 180°C for 25 min after addition of different amino acids by 42% to 70%; this probably resulted from competitive

consumption of acrylamide precursors. Another reason could be an elimination of acrylamide by nucleophilic components in the amino acids. Soaking of potato slices into glycine or lysine solutions also resulted in a reduction of the acrylamide levels by 45% to 94% depending on the type of amino acid, the concentration of the solution (0.1%, 0.5% and 1%) and the duration of soaking (1 min, 3 min and 5 min) (Kim, Hwang, and Lee 2005). The reduction of acrylamide was strongly correlated with the concentration of amino acid and the duration of frying.

Ciesarová, Kiss, and Bögl (2006) showed that the use of the enzyme L-asparaginase (type EC 3.5.1.1) at a concentration of 0.2 units of lyophilized enzyme per gram of fresh potato mash at an incubation temperature of 20°C resulted in a reduction of the acrylamide content in the fried product of about 50% at a frying temperature of 180°C for 20 min. L-asparaginase catalyzes the hydrolysis of asparagine into aspartic acid and ammonia, which results in the elimination of one main precursor necessary for the acrylamide formation from the system before heating. With a larger amount of enzyme (2 U/g) and a higher incubation temperature (37°C), it was possible to reduce the content of acrylamide in the product by about 97%. The authors concluded that the application of L-asparaginase could be a successful way to strongly reduce the content of acrylamide in fried products. Therefore, they protected the procedure by the patent application filed with the Industrial Property Office of the Slovak Republic under the number 5027-2006.

Different authors showed that the use of antioxidants could reduce the content of acrylamide in fried potato products. Zhang et al. (2007) used antioxidants of bamboo leaves to reduce the content of acrylamide in potato crisps and French fries. They immersed the raw material into solutions with different contents of the antioxidant before processing and found a reduction of the acrylamide content of about 75% in potato crisps and French fries when the antioxidant ratio was 0.1% and 0.01% (w/w), respectively in comparison with a control without antioxidants from bamboo leaves. The optimal inhibition rate was obtained when the immersion time was 60 s. In this case, the sensory evaluation of the products with regard to crispness and flavor was maintained, while the content of acrylamide was reduced drastically. Becalski et al. (2003) showed that the addition of rosemary herbs to olive oil or corn oil reduced the formation of acrylamide by about 25%, and Fernández, Kurppa, and Hyvönen (2003) found a reduction of acrylamide of about 50% after addition of a flavonoid spice mix.

#### 7.3.2.3 Frying Equipment

A further important point in the development of strategies to reduce acrylamide in fried food is the design of the frying equipment. The usual fryer equipment consists of a basin for the frying medium, a heating source, and a basket for the frying material. The heating source is one of the most sensitive parts of the equipment for the formation of acrylamide in the product because research has shown the dependence of acrylamide development with increasing temperature. Thus, it is important that a consistent transfer of heat from the heating source to the product is ensured during the process. It is also important that the setting of the temperature is exact. For most household fryers, setting of the temperature is possible only in a wide range, which results in great differences in acrylamide contents at supposed comparable temperatures. The

industry is asked to produce more precise temperature-control systems for household and professional frying systems.

The ratio between the product being fried and the frying medium is another important setting for the production of food low in acrylamide. In collaboration with cooking experts with the aim to reduce the formation of acrylamide in French fries to < 100 µg/kg, Grob et al. (2003) suggested a "10% rule" describing the addition of 100 g product to 1 L of oil. As parameters for the relevant temperature for acrylamide formation, they defined initial oil temperature, thermal mass of the fryer, heating capacity of the fryer, heat-transfer characteristics of the oil, and the amount of potatoes in comparison with the amount of oil. Grob et al. (2003) showed that the temperature of the frying medium dropped by 20–35°C after the addition of cold raw material. Then, the heater started, but was unable to compensate the loss of heat resulting from the cooling effect of the potatoes and water evaporation. Only if the initial temperature of the fryer was sufficiently high (170°C) and the amount of product appropriate (product: oil ratio of 1:10), was it possible to ensure a high product quality with a low amount of acrylamide and a high sensory quality. With a lower ratio between product and oil, e.g., 1:5 (200 g French fries/L oil), the temperature drop became more drastical, with the consequence that the heater could not compensate for this drop within the frying time, resulting in soft and oily French fries that were not accepted by the consumer. Thus, the authors recommended that only an amount of potatoes should be added to the fryer, which keeps the oil temperature towards the end of the process above 140°C. According to the 10% rule, 10% potatoes referring to the oil should be a good compromise between efficiency and temperature control.

An interesting possibility to reduce acrylamide formation during frying is the application of low pressure (vacuum) during the process. Granda, Moreira, and Tichy (2004) and Granda and Moreira (2005) showed that frying under vacuum (10 Torr) reduced the acrylamide content in potato chips fried to the same final moisture content of 1.5% for about 94% in comparison with those fried under normal (atmospheric) conditions. They concluded that different acrylamide contents obtained in traditional and vacuum frying mainly depended on the different temperatures used for the processes. During traditional frying, temperatures between 150°C and 180°C are in use, while the temperature range for vacuum frying is between 118°C and 140°C, resulting in an exponential increase of the acrylamide content with frying time, but at lower levels than for traditional frying. From these results, the authors recommended that vacuum frying is the only technology available that can produce high-quality potato chips with no acrylamide content.

## 7.4 CONCLUSIONS

The real effect of acrylamide taken up by food on the health of human beings is not clear, but according to the recommendation of the "ALARA (As Low As Reasonably Achievable) principle", research institutions, authorities and industries have undertaken vigorous efforts to change the process of deep-fat frying to reduce the content of acrylamide in products. The main problem is that acrylamide formation also follows the mechanisms of the Maillard reaction, which is responsible for the formation of many desirable components necessary for a pleasant taste and smell of the product

as accepted by the consumer. Thus, it is important not to lose sight of the quality of the product during research and development of new strategies with the aim to reduce the concentration of acrylamide in ready-to-eat food.

In the five years since the first announcement of the finding of acrylamide in fried, baked, roasted and deep-fat fried foods, a lot of research and new developments was implemented with the result that the content of acrylamide in most products has been strongly reduced.

In the process of deep-fat frying in general, the use of three different setscrews is conceivable for the reduction of acrylamide: raw material, production process, and the equipment of the process. The chapter has shown some promising possibilities, which in the meantime partially were taken over in the processing, such as reduction of processing temperature, increase of the final moisture content in potato crisps, choice of definite raw material or diverse possibilities of a pretreatment of the raw material before processing. As shown by various authors (Granda, Moreira, and Tichy 2004; Grob et al. 2003), the combination of different steps results in a drastical reduction of acrylamide in fried products not only in the laboratory, but also in practice. It will probably not be possible to reach 0% acrylamide content in the product (which would be desirable from a health viewpoint) because the quality of the product would be changed dramatically, resulting in rejection by the consumer. Even so, the examples given in the chapter show that many methods are available to bring the content of acrylamide in fried products to a lower level.

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# 8 Microstructural Changes During Frying of Foods

*Michael Ngadi, Akinbode A. Adedeji, and Lamin Kassama*

## CONTENTS



## 8.1 INTRODUCTION

Food products undergo several chemical, nutritional and physical changes during deep-fat frying. Starch components are gelatinized, proteins are denatured, some nutrients are destroyed, various flavor components are developed, crusts are formed and pores are developed to form unique microstructures during the frying process (Moreira and Barrufet 1996). These changes combine to give fried foods their unique textural and sensory characteristics which have been difficult to replicate using any

other unit operation. Frying is a simultaneous heat and mass transfer process. Oil acts as the heating medium and facilitates mass transfer. Heating occurs from the surface into the interior of the food material by convection and conduction modes of heat transfer. The overall product temperature is increased, leading to formation of water vapor which burrows its way to the surface of the product due to a pressure and concentration gradient, leaving behind pores that become significant in subsequent oil absorption. Heat also causes caramelization of sugars and induces reactions between amino acids and reducing sugars, creating the brown or golden coloration and hardness of the crust that are characteristics of some fried foods. Further, there are significant changes in the volume of the final product due to shrinkage at the elevated temperatures during frying.

There have been substantial attempts to understand the changes that occur during deep-fat frying at the macro level, but several of these changes occur at micro levels. Thus, it is vital to examine microstructure evolution in fried products to develop techniques that would enhance their effective study and control. Techniques that are used in medical, biological and material sciences to study materials at the micron scale have recently being adapted to study foods (Aguilera 2005). Microscopy techniques and X-ray imaging have been used to some degree. Advances in computer image analysis have also enhanced the digital and quantitative analysis of the obtained image dataset. The contribution of these techniques in the study of microstructural changes during food processing such as frying is considerable.

In this chapter, the focus is on reviewing the microstructural changes during deep-fat frying. We present various modern approaches to studying food microstructures and illustrating how quality is affected by microstructural changes.

### 8.1.1 Deep-Fat Frying

Deep-fat frying is considered to be one of the commonest and oldest forms of food preparation. It may have originated from the Mediterranean region (Varela 1988). Fried products are now found all over the world with increasing popularity. Deep-fat fried foods combine unique flavor with special textural characteristics. The process is set up to seal and modify the food surface by immersion in hot oil to preserve the flavors and retain the juiciness in a crispy crust while simultaneously ensuring that the food is cooked properly for easy mastication and digestion. During frying, food materials undergo internal and external structural changes that greatly influence quality.

There are concerns about weight disorders and related health problems associated with high consumption of high-fat foods. Various approaches have been adopted with different degrees of success to control oil absorption during frying. Pre-frying treatments and modification of food surfaces by application of coating are among the promising techniques for reducing fat intrusion during frying. The mechanism of control in most cases has been related to structural modification of the products by the various process strategies. The distribution of pore evolution and pore size is greatly modified by these methods of control (Aguilera and Stanley 1999). Knowledge gained by understanding the interacting factors should provide tools for optimization of the deep-fat frying process.

### 8.1.2 Heat and Mass Transfer

Typical frying oil temperatures are between 150–190°C. Cooking initiates immediately after a product is dropped into hot oil. The rate of heat transfer is influenced by the composition and appropriate heat and mass transfer properties of the food, including thermal conductivity, thermal diffusivity, specific heat and density, and diffusivities. These properties change during the frying process. The temperature gradient between food product and the frying oil, and the resulting convective heat transfer coefficient, are the major determinants of the heat transfer rates between the frying medium and the food product. The heat transfer coefficient is greatly influenced by the complicated interactions at the food–oil interface. These interactions are mainly due to the bubbling caused by the evaporation of water from the food product to the oil (Singh 1995) as well as the complicated structural and textural changes occurring in the product. Farkas, Singh, and Rumsey (1996) observed that during frying of a slab-shaped, high-moisture product, the temperature within the fried food was restricted to the boiling point of water due to moisture. However, for thinner, medium-to-low moisture and more structurally intact products, there are indications that internal temperatures may exceed the boiling point of water during frying.

Moisture loss and oil uptake are the two major mass transport phenomena during deep-fat frying. These mass transfer processes are coupled to the heat transfer process. One of the fundamental approaches in describing mass transfer during deep-fat frying has been to assume that oil uptake and moisture loss are controlled by diffusion. The mass transfer process taking place during deep-fat frying is a function of frying time and temperature. The instantaneous rate of mass transfer at any time tends to be proportional to the mass content at that instant. Ni and Datta (1999) found that moisture transfer rates increase significantly with high initial moisture because surface evaporation and subsequent internal evaporation are higher for foods with higher moisture. Oil uptake and moisture loss may increase with increasing frying temperature, although reports in the literature are varied. Blumenthal (1991) used a water-soaked sponge to simulate the coupled heat and mass transfer mechanisms in deep-fat frying. The author described how water migrates from the internal parts of the product to the surface due to the dehydrating effect of frying. As moisture migrates outwards, an opposite inflow of oil take places by diffusion to fill up the pores created by moisture loss. These two transfer phenomena have been described as simultaneous events by some authors (Datta 2007; Farid and Butcher 2003; Gamble, Rice, and Selman 1987; Ngadi, Dirani, and Oluka 2006; Pinthus, Weinberg, and Saguy 1993) whereas there are reports that oil intrusion occurs during the cooling phase after frying (Moreira, Sun, and Chen 1997). In an extensive study with French fries, Krokida, Oreopoulou, and Maroulis (2000a), reported similar kinetics for moisture and oil transfer. Moisture content was negatively affected by oil temperature. Gamble, Rice, and Selman (1987) attempted to describe the relationship and mechanisms of oil uptake and moisture loss during frying. The authors suggested that the moisture loss takes place due to a diffusion gradient between the dry surface and wet core of the food, and also due to pressure gradient created by the evaporation of the inner moisture. However, for the steam to escape through the food it has to find "selective weaknesses" in the food structure. Thus, enforcing the food structure

would reduce moisture loss and eventually reduce oil uptake. Krokida et al. (2001a) recorded that moisture loss and fat absorption in French fries can be changed by pre-drying before frying. The pre-frying process modifies the structural characteristics of the product, resulting in changes in moisture and fat transfer. Coating the food product can also provide a protective and reinforcing barrier for the food product.

The degree of moisture loss and fat uptake are very important quality indicators for fried foods in terms of health concerns and palatability of the products. It is desired in some product (e.g., tortilla and plantain chips) that as much moisture is removed as possible to give the product a unique crispy texture, while in others (e.g., breaded chicken nuggets and French fries), retention of sufficient moisture is desired for juiciness and chewability of the products, respectively. Structural changes in these products have an important role in defining heat and mass transfer characteristics and subsequently the quality of the product.

### 8.1.3 Crust Formation

Crust formation is an important contributor to the unique textural profile of products developed during deep-fat frying. The characteristic crispy or crunchy texture and the brown or golden color of fried foods are direct consequences of moisture evaporation, dehydration, chemical reaction from browning (Maillard reaction), caramelization and crust formation that occur mostly at the food surface during frying. The elevated temperature during frying causes the surface temperature of the product to rise, leading to moisture evaporation which recedes inward as frying progresses. Thus, it is a moving boundary process with an interface that separates the core and the crust proceeding from the surface to the inner part of the food during frying (Ngadi, Watts, and Correia 1997). Ateba and Mittal (1994) used a very simple linear model to predict the development of crust thickness in meatballs. Crust was assumed to form at locations with temperatures $\geq 100°C$. The authors reported good agreement between experimentally measured and predicted crust growth rate.

The formation of crust is a significant quality index for fried foods. Crust plays a major part in mass transfer during deep-fat frying by reducing oil uptake and moisture loss within the inner food matrix, thus contributing to the juiciness and chewability of fried foods. The dried-out crust forms a barrier to mass transfer. A good relationship was established between crust formation and mass transfer. It has been reported that most oil absorbed during frying of French fries is located in the crust, typically at a depth of 1–2 mm below the surface of the product (Farkas, Singh, and McCarty 1992; Moreira, Castell-Perez, and Barrufet 1999). Some materials such as hydrocolloids and some flours are capable of gelling to form barriers, and have been used to coat certain fried foods. The use of these coatings to form special crust has been effective in controlling mass transfer during frying (Fiszman and Salvador 2003; Garcia et al. 2004; Pinthus, Weinberg, and Saguy 1993). Crust characteristics such as color, surface roughness, depth and texture are functions of several factors, such as the food constituents, the frying temperature and duration, and the quality of frying oil. There is sufficient evidence that crust structural characteristic is the main factor influencing mass transfer during frying (Aguilera and Gloria 1997; Pinthus, Weinberg, and Saguy 1995a). Pinthus, Weinberg, and Saguy (1995a) reported an increase in crust yield strength of restructured potato product with frying time and

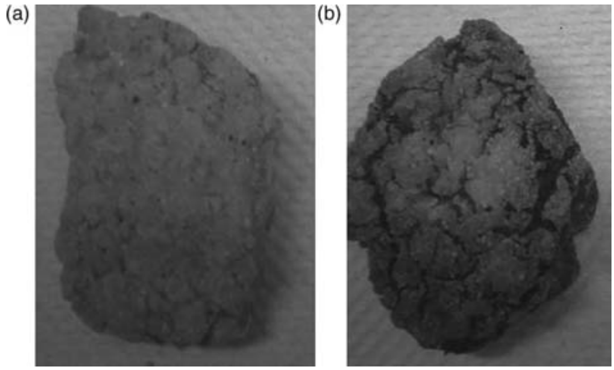



**FIGURE 8.1** Crust surface of microwave precooked deep-fat fried chicken nuggets (a) after 30 s and (b) after 90 s of frying in canola oil.

a positive correlation between crust yield strength and porosity. In this study, porosity of restructured potato product decreased with frying time unexpected, due to oil infiltration into pores, capillaries and voids initially filled by air or steam generated during frying.

The development of surface roughness is a unique characteristic of crust formed during frying. The initial moisture content, pretreatment, food components and frying conditions are among the factors that influence the degree of surface roughness developed during frying. Figure 8.1 shows images of chicken nuggets with increased surface roughness due to pre-frying processing (microwave pre-cooking) and longer frying time. Surface roughness and increased oil uptake have been shown to have a positive correlation (Saguy and Pinthus 1995; Thanatuksorn et al. 2005). The increased contact surface due to surface roughness may be responsible for the increase in oil absorption. Further, surface roughness may play a part in modifying heat transfer coefficients, with consequences on heat transfer rates during frying. Qiao et al. (2007) used an imaging-based technique to predict the mechanical properties of chicken nuggets fried at different times. The mechanical parameters studied included maximum load, energy to break point and toughness of the fried chicken nuggets. The study established the strong potential for assessing structural and textural characteristics of fried products by considering crust surface image indices.

### 8.1.4 Shrinkage

Fried foods experience changes in their structural matrixes due to the intensity of frying heat. Shrinkage occurs during frying as a result of drying out of moisture from the frying product, causing collapse of its structural framework, which eventually manifests as volume reduction. The rate of water removal influences the degree of shrinkage (Aguilera and Stanley 1999). Slow moisture evaporation will result in uniform reduction in volume. However, if the rate of moisture removal is high, the surface crust forms quickly, creating a solid crust that preserves the original shape of the product to some degree, but leads to the interior part forming voids and cracks depending on the initial moisture content of the product.

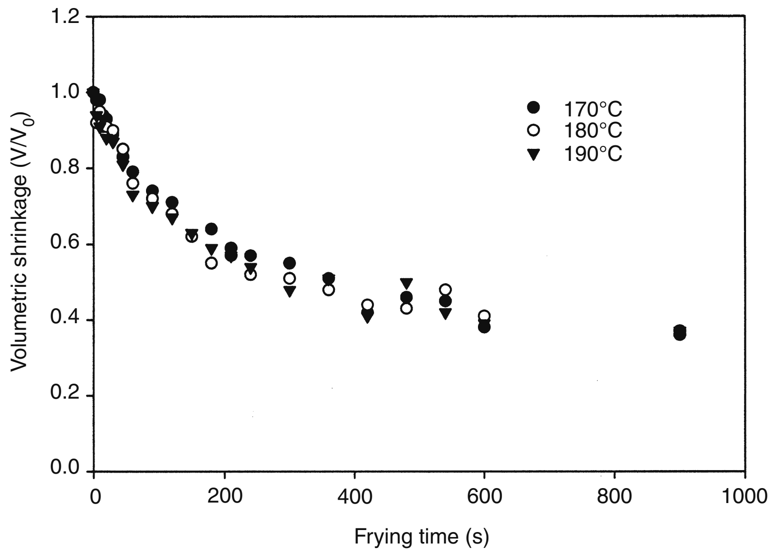



**FIGURE 8.2** Volumetric shrinkage of chicken breast meat as affected by frying time and temperature (Kassama and Ngadi 2003).

Kassama and Ngadi (2003) reported an exponential decrease in volumetric shrinkage of de-boned chicken breast meat during frying (Figure 8.2). The initial period of frying of up to 90 s showed that shrinkage occurred rapidly, but gradually decreased after 300 s of frying. This was attributed to the possibility of oil absorption at regions of low moisture content. A linear correlation was observed between moisture loss and shrinkage. The effect of temperature on shrinkage was not so distinct, showing no significant difference for the fried chicken breast meat. Kawas and Moreira (2001) reported a significant influence of different pre-frying treatments on the shrinkage of tortilla chips. Steam-baked, control and freeze-dried tortilla chips experienced reduction in volume at various degrees. Similarly, Shyu, Hau, and Hwang (2005) reported various effects of chemical and physical pretreatments on shrinkage of vacuum-fried carrot chips. It was concluded that the best pretreatment method to give the least shrinkage and oil absorption during frying was fructose immersion and freezing prior to vacuum frying. Thus, process strategies that strengthen the structural matrix of food products and lessen the severity of the frying process tend to reduce shrinkage because shrinkage is related to structural collapse.

## 8.2 PORE DEVELOPMENT AND STRUCTURE

The development of pores is a major structural change during deep-fat frying. Evaporation of moisture from food product during frying creates capillary paths on its way out of the product. Intense heat could lead to explosive evaporation that brings about formation of large pores and crevasses, especially if there is quick formation of crust. Thus, crust formation influences pore development. When crust is formed quickly, it creates a barrier to evaporation. As frying intensifies, the vapor pressure build-up due to the crust barrier leads to expansion at different core locations and to sudden

vaporization that creates large pores (Bhat and Bhattachacharya 2001; Mellema 2003; Shyu, Hau, and Hwang 2005). The chemical and physical transformation of food components such as leavening of starch (from $CO_2$ production) and its gelatinization, and protein denaturation that occurs in the form of swelling or shrinkage, also contribute to the spatial network characterized as pores in fried foods (Llorca et al. 2001). The gelatinized starch is usually dispersed in the continuous phase formed by the denatured protein and together they form an association of strands. This gives fried foods a distinct morphological pattern that affects the general quality.

Pre-process treatment and the intensity of frying, coupled with the initial moisture content of the food product, have considerable influence on the final pore structure. For instance, large-diameter pores were observed in an overcooked, deep-fat fried tortilla chip, and the pores were saturated with oil (McDonough et al. 1993). In general, three types of pore structures are identified in porous solids based on their connectivity: interconnected pores; isolated or non-interconnected pores; and "dead-end" or "blind pores" (Figure 8.3). Interconnected pores are usually accessible from many directions. They contribute to the transport of fluid across the porous medium. Blind or dead-end pores are accessible from one direction only. Their influence on flows within the pore network is limited. Non-interconnected pores are inaccessible islands buried in the solid matrix of the porous material and behave as part of the solid (Dullien 1992). Isolated pores therefore decrease the diffusivity characteristics of the porous medium.

The pore structure of a fried food influences its mechanical properties and thus its acceptability in terms of texture (Clayton and Huang 1984). Texture and friability are also influenced by pore size distribution and sizes of the capillaries. Pore structure has a profound influence on the macroscopic and microscopic properties of fried food. Pore structure could be defined in terms of macroscopic and microscopic parameters. Macroscopic pore structure parameters describe the overall pores constituting the

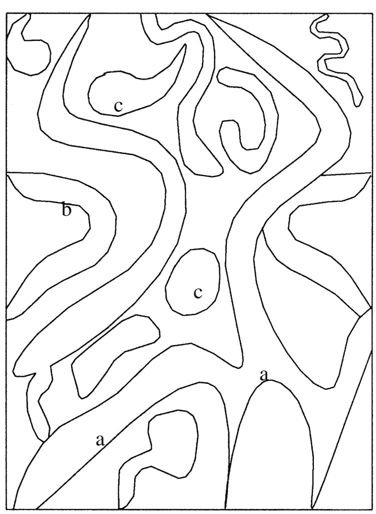



**FIGURE 8.3** Illustration of different types of connectivity in a porous structure. (a) Interconnected pores; (b) dead-end or blind pores; and (c) isolated or non-interconnected pores.

main skeleton of the pore network, whereas microscopic pore structure parameters refers to the pore sizes (diameter, volume), pore-size distribution and the volume distribution functions (Dullien 1992). The macroscopic pore structure is more closely related to the transport characteristics of the porous medium. Microstructural pore structure parameters provide more fundamental information on the pore structure network and define the macrostructural parameters.

### 8.2.1 Macroscopic Pore Structure

The most important macroscopic pore parameters are density, porosity, specific surface area and breakthrough capillary pressure.

#### 8.2.1.1 Porosity and Density

Density is the mass of a quantity of matter per unit volume of the same quantity. Although density is a relatively simple parameter and widely used in food process analysis, it can be confusing because density can be defined from different perceptions. The true, skeletal or solid density, also referred to as "absolute" or "particle" density, refers to the density calculated on the basis of the volume excluding the pores that may be in the volume, and the interparticle spaces. The apparent density (envelope density) is based on the volume including the pores, but excluding the interparticle spaces. In other words, apparent density measures blind and non-interconnected pores in a sample and excludes open, interconnected and interparticle pore spaces. The bulk density rests on volume measurement including the pores and the interparticle spaces. The difficulty of interpreting density terms reported from different research reports stems from difficulties in accurately measuring the pores and interparticles spaces in products.

Several researchers used (air or helium) pycnometer or mercury porosimetry technique to measure absolute densities (Kassama and Ngadi 2001; Kassama, Ngadi, and Raghavan 2003; Karathanos, Kanellopoulos, and Belessiotis 1996). Helium pycnometry is essentially a displacement technique and a sample volume is calculated from the observed pressure change that the gas undergoes when it expands from one chamber containing the sample into another chamber (expansion chamber) without the sample. Gas fills all open spaces, including that of the pores. Helium is the preferred gas for measuring absolute density because it can penetrate most of the pores in food materials due to its minute atomic radius (3 Å) (Chang 1988; Karathanos, Kanellopoulos, and Belessiotis 1996; Karathanos and Saravacos 1993). Bulk density is generally measured by liquid displacement. The property is problematic to measure for most porous fried foods. An acceptable technique is to use non-penetrating liquids or to cover the sample with light silicon grease to make it impervious during liquid displacement tests. Alternatively, the test could be conducted quickly to allow no time for a penetrating liquid to penetrate into the pores of samples. Krokida, Oreopoulou, and Maroulis (2000b) used n-heptane, Moreira, Castell-Perez, and Barrufet (1999) used toluene, and Hicsasmaz and Clayton (1992) used fine sand to measure the bulk densities of various foods. A simple volume displacement apparatus (Figure 8.4) has been used by Kassama (2003) and Kassama and Ngadi (2003) to measure bulk density of deep-fat fried foods. The system consists of a sample

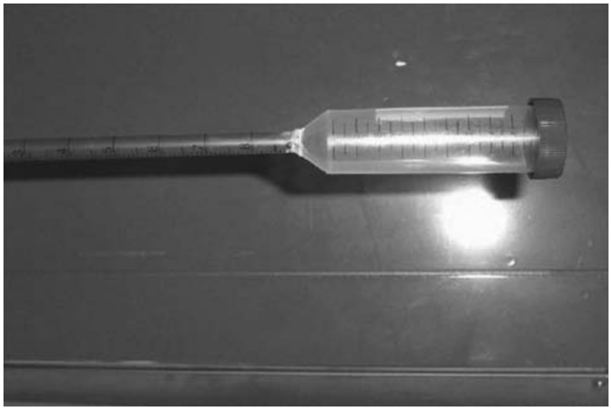


**FIGURE 8.4** Simple volume displacement pycnometer for measuring bulk volume of food product.

compartment, lid and burette with graduations. The apparatus was filled with water and the samples immersed in the sample compartment, which was then hermetically sealed with the lid. The volume displacement was measured by inverting the apparatus twice, the first time without the samples and the second time with the samples immersed in the liquid. Samples are immersed in the top compartment and sealed. When inverted, the displaced volume is determined. Bulk and particle densities of deep-fat fried de-boned chicken meat samples are shown in Figure 8.5 and Figure 8.6. The figures indicate that bulk density decreased with frying time, whereas the apparent density increased with frying time. Air-drying of potato displayed a similar trend (Wang and Brennan 1995). Frying oil temperature and time have a dramatic effect on the structural changes of food products.

The bulk density values decrease from 1.15 g/cm³ for the control (for which there is no moisture loss) to 0.98, 0.95, and 0.92 g/cm³ after 900 s of frying at the frying oil temperatures of 170, 180, and 190°C and final moisture contents of 33, 25, and 16% wet basis (w.b.), respectively. Frying at a higher temperature resulted in a lower bulk density. This was attributed to the effect of aggravated mass transfer effects, i.e., water loss and oil uptake, resulting in shrinkage and pore formation. Rahman et al. (1996) reported similar observations on air-drying of fish muscles. In contrast with bulk density, the apparent density increased consistently from the initial value of 1.13 g/cm³ to 1.21, 1.29, and 1.23 g/m³ when fried for 540 s at 170, 180, and 190°C, respectively. This behavior was analogous to the oil absorption curves during deep-fat frying (Kassama and Ngadi 2001). The change in density could be attributed to the physicochemical reaction, which may have induced deterioration of solid contents and the collageneous connective tissues, similar to protein denaturation. The increase in apparent density could also be attributed to the mass transfer process that occurred during deep-fat frying. During this process, as moisture evacuates, the solid volume may decrease as a result of shrinkage due to deterioration of connective tissues, and denaturation of protein may also contribute to increase the apparent density. The increasing trend in apparent density (or decreasing trend in bulk density) was observed in the 0–540 s region of frying for all frying oil temperatures, after

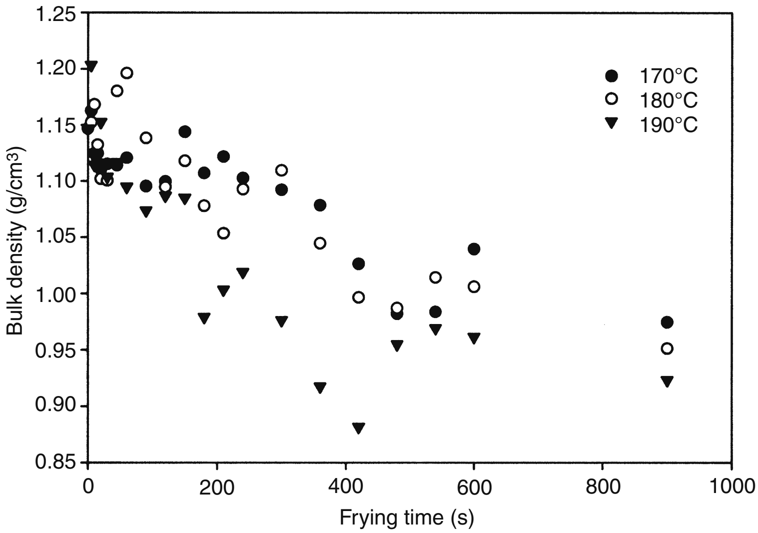



**FIGURE 8.5** Bulk density as a function of time for de-boned chicken meat deep-fat fried at 170, 180, and 190°C.

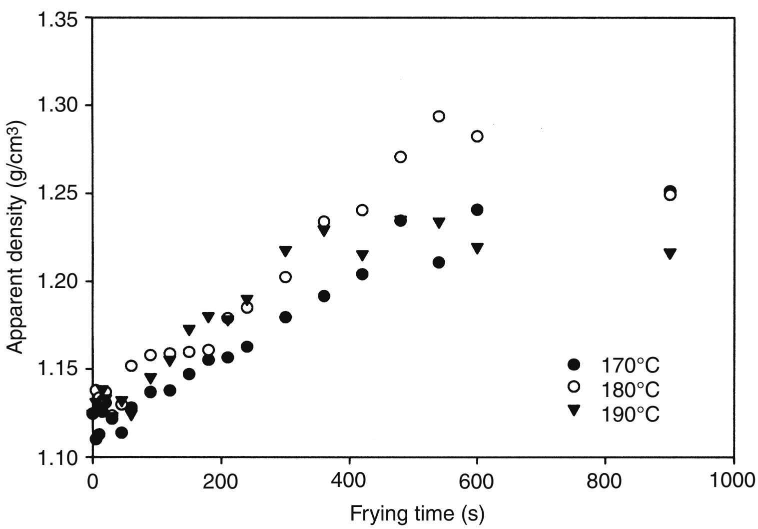



**FIGURE 8.6** Apparent density as a function of time for de-boned chicken meat deep-fat fried at 170, 180, and 190°C.

which the values tended to equilibrate. The change in state could be attributed to oil saturation in the empty voids. Krokida et al. (2001a) also reported equilibrium moisture content for fried potato strips. For these products, the authors reported similar kinetics of change in bulk density and apparent densities (referred to by the authors as apparent and true densities, respectively).

Porosity, also referred to as "voidage", is the fraction of the bulk volume of a porous medium that is occupied by pores or void spaces:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_s} \tag{8.1}$$

where, $\varepsilon$ porosity, $\rho_b$ bulk density, and $\rho_s$ is solid density.

Porosity values may vary from near zero to unity. It indicates the open structure of the fried product. Porosity and bulk density of deep-fat fried restructured potato have positive correlation while the particle density has a negative correlation with porosity (Pinthus, Weinberg, and Saguy 1995b). The authors also reported an increase in oil uptake as porosity increased. Similarly, Kassama and Ngadi (2003) reported an increase in porosity with frying of chicken breast meat (Figure 8.7). The porosity development appeared to follow the oil uptake profile. The leveling off in porosity at longer frying times could be attributed to oil uptake. Pinthus and Saguy (1994) suggested that the intrusion of oil in voids left by evacuated moisture hinders pore development. The absorbed oil may also minimize structural collapse. Moreira, Palau, and Sun (1995) and Moreira, Sun, and Chen (1997) reported that bulk density of tortilla chips decreased, while their porosity and oil uptake increased as frying progressed. Krokida, Oreopoulou, and Maroulis (2000b) presented an increasing trend in porosity with frying time in the study of French fries, and this was also corroborated by Kawas and Moreira (2001) in their study of tortilla chips.

Some authors reported different trend for porosity with frying time. Pinthus, Weinberg, and Saguy (1995a) recorded a decreasing trend for porosity in deep-fat fried restructured potato crust with different gel strengths. Thus, porosity could depend on the deformability modulus (gel strength) of products. This decreasing

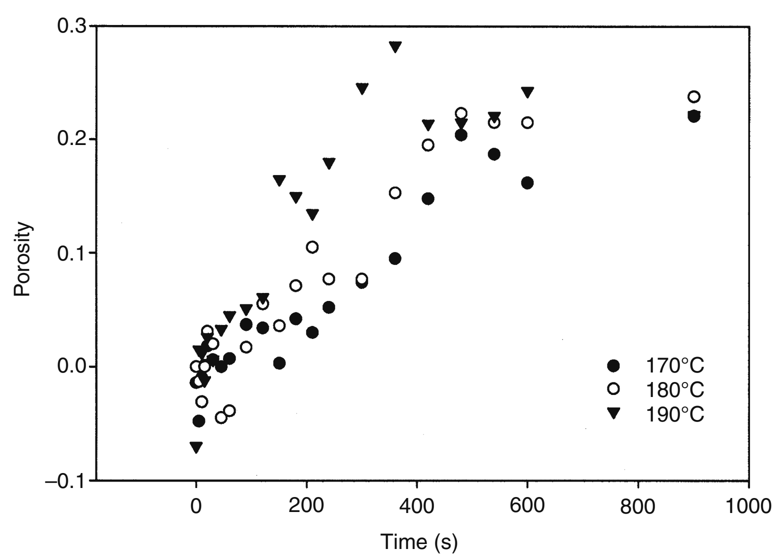



**FIGURE 8.7** Change in porosity with frying time at different temperatures in de-boned chicken meat slabs.

trend in porosity was suggested to be due to oil filling the pores and capillaries that were initially occupied by steam and air generated by water evaporation (Pinthus and Saguy 1994). Porosity measurements on fried and freeze-dried chicken meat samples showed decreasing porosity values with increasing frying times (Kassama and Ngadi 2005). Although structure formation in fried foods is a complicated phenomenon, it is expected that porosity may increase with increasing frying time because moisture is lost during the frying process, which should create pore spaces within the food material. The decreasing trend reported by some authors could be a result of not accounting for the oil intrusion in the calculation of porosity. The methodology used to estimate porosity is vital to correct interpretation of porosity values. For instance, porosimetry requires sample preparation involving drying the samples before measurement of porosity. Thus, the resulting porosity values are for the dried state of the samples. The dried samples should have more pores because moisture has been evacuated.

Porosity values obtained by porosimetry techniques are higher than those obtained using pycometry methods. It should be possible to adjust raw porosity data obtained from porosimetry methods to account for the moisture evacuated. This approach has not yet been reported. There is therefore a need for more studies with different methods to clarify available porosity data reported in the literature. Table 8.1 presents pore size distribution and porosity for some fried products.

#### 8.2.1.2 Pore Surface Area

The surface area of a pore is the interstitial surface area of the voids. It is defined per unit mass or per unit bulk volume of the porous material. It plays an important part in various applications involving porous foods. Specific surface area determines the adsorption capacity of various food products. Thus, it influences the effective fluid conductivity, permeability, hydration and rehydration ability of various products (Dullien 1992; Rahman, Al-Amri, and Al-Bulushi 2002). Measurement of pore surface area presents greater difficulty than straight measurement of porosity or pore sizes. The commonest method of measurement is by mercury porosimetry techniques. Specific surface area of the pores (S) can be estimated from the mercury intrusion data by integrating the distribution curve of the cumulative volume of mercury intruded into a sample in a given pressure range assuming all pores are filled and that the pores are cylindrical (Karathanos and Saravacos 1993; Kassama and Ngadi 2005; Panchev and Karageorgiev 2000).

$$S = \left[\frac{1}{\gamma \cos\theta}\right]^{v} \int_{0}^{F} P_i dV = \left[\frac{1}{\gamma \cos\theta}\right] \sum P_i \Delta V_i \tag{8.2}$$

where, $\Delta V_i$ is the volume of penetrated pore between two pressures $P_i$ and $P_{i+1}$.

Surface area could also be estimated from gas sorption isotherm data. The amount of gas adsorbed by a porous food product is determined as a function of pressure (or water activity) and the surface area can be estimated from the BET equation (Bluestein and Labuza 1972; Iglesias, Chirife, and Viollaz 1977; Kanel and Morse 1979; Lowell and Lowell 2004). Care must be taken when interpreting or

**TABLE 8.1**
**Pore Parameters for Different Deep-Fat Fried Foods**

| Fried samples | Process condition | Measurement methods | Pore size (μm) | Porosity | Reference |
|---|---|---|---|---|---|
| Restructured potato crust | Samples were pretreated (freezing and fried at 170°C for up to 5 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by 100-μm diameter glass beads<br>Particle density: helium pycnometer | – | 0–0.180 | Pinthus, Weinberg, and Saguy (1995a) |
| Restructured potato | Samples were pretreated (fluctuating sub-freezing and fried at 170°C for up to 5 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by 100-μm diameter glass beads<br>Particle density: helium pycnometer | – | 0.090–0.410 | Pinthus, Weinberg, and Saguy (1995b) |
| French fries | Samples were pretreated (blanching and fried at different temperatures; 150, 170 and 190°C for up to 20 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by n-heptane<br>Solid density: helium pycnometer | – | 0.010–0.500 | Krokida, Oreopoulou, and Maroulis (2000b) |
| French fries | Samples were pretreated (blanching, osmotic soaking and fried at 170°C for up to 15 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by n-heptane<br>Solid density: helium pycnometer | – | 0.001–0.610 | Krokida et al. (2001b) |
| French fries | Samples were pretreated (blanching, drying and fried at 170°C for up to 20 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by n-heptane<br>Solid density: helium pycnometer | – | 0.000–0.720 | Krokida et al. (2001c) |
| Sweet potato | Samples were pretreated (blanching, freezing, dehydration and fried at 170°C for up to 5 min) | Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by water<br>Solid density: helium pycnometer | – | –0.410–0.350 | Taiwo and Baik (2007) |

(*continued*)

**TABLE 8.1** (*continued*)

| Fried samples | Process condition | Measurement methods | Pore size (μm) | Porosity | Reference |
|---|---|---|---|---|---|
| Tortilla chips | Samples were pretreated (freeze-dried and steam baked) and fried at 190°C for up to 1 min | Pore size: image analysis.<br>Porosity: ratio of bulk and solid densities<br>Bulk density: volume displacement by toluene<br>Solid density: helium pycnometer | 25–300 | 0.330–0.700 | Kawas and Moreira (2001) |
| Coated carrot | Samples were coated with gum and fried at 170°C for up to 4 min | Porosity: ratio of bulk and solid densities.<br>Bulk density: volume displacement by paraffin.<br>Solid density: nitrogen gas pycnometer | – | 0.040–0.245 | Akdeniz, Sahin, and Sumnu (2006) |
| Beefburgers | Samples were frozen (–21°C) and fried at 175°C up to 137 s or till the center of the sample reached 72°C | Porosity (density): ratio of measured and calculated densities<br>Porosity (shrinkage): ratio of volume due to water and fat loss and volume due to shrinkage<br>Measured density: volume displacement by rapeseed oil<br>Calculated density: summation of the ratio of individual component density and the weight fraction | – | Density based porosity: 0.009–0.18<br>Shrinkage-based porosity: 0.05–0.35 | Oroszvari et al. (2006) |
| Chicken meat | Samples were fried at 180°C up to 360 s and freeze-dried | Porosity: ratio of bulk and solid densities<br>Pore size, bulk and solid densities: mercury intrusion porosimetry | 0.006–10.2 | 0.370–0.710 | Kassama and Ngadi (2005) |
| Chicken nuggets breading coating | Samples were fried at 180°C for up to 4 min | Pore size, porosity, pore shape and pore interconnectivity: 3D image analysis. | 0.010–400 | 0.010–0.301 | Adedeji and Ngadi, (2007) |

comparing surface area data from different studies obtained by different measurement techniques. For instance, in water vapor sorption studies, water is adsorbed not only on the pore surfaces, but also on water-binding sites such as glucose residues, which may present error in surface area values. Farkas and Singh (1991) reported that the surface area of air-dried chicken meat samples were lower than those of freeze-dried samples. However, the authors reported that values of surface areas did not considerably influence rehydration properties of the dried samples. There is very scarce information on pore surface areas of fried foods.

Kassama and Ngadi (2005) showed that pore surface area of fried chicken meat increased with increasing frying time. The cumulative pore surface area of non-fried chicken samples was 6.92 $m^2/g$ compared with 8.24 $m^2/g$ for samples fried at 180°C for 360 s. Fortuna et al. (2000) examined pore characteristics of potato, wheat and corn starches. The authors observed that specific pore surface area of the starch granules was related to their pasting temperature and maximum viscosity. Thus, it appears that the size of pores and their specific surface areas can significantly influence their thermal and physiochemical properties. This finding may have interesting implications for breaded fried foods, which typically uses starch-based coatings.

#### 8.2.1.3 Breakthrough Pressure

The breakthrough capillary pressure (also referred to as the "bubble pressure" or "threshold pressure") is an important macroscopic property of porous media. It is the pressure required to establish a continuous penetration pathway in a porous solid by a non-wetting phase through a networks of capillary tubes of randomly distributed diameters. Thus, breakthrough pressure indicates the pressure at which the penetrating fluid becomes hydraulically conductive in the macroscopic sample. It is normally related to permeability in porous solids. In mercury porosimetry, breakthrough capillary pressure is identified as the pressure corresponding to about 10–20% non-wetting phase saturation or the point of inflection in the drainage capillary pressure curve. The parameter can be used to compare the influence of different treatments on porous samples.

### 8.2.2 Microscopic Pore Structure

Characterization of microscopic pore structure in foods is extremely challenging due to the peculiar geometry of pore structures and the complexity of food products. Mercury porosimetry, gas sorption or microscopic imaging are typically used to determine microscopic pore structure parameters. Microscopic pore structure parameters include pore size (diameter, volume), pore size distribution, and the volume distribution function. Pore size may be defined as a portion of a pore space bounded by solid surfaces. Although a relatively simple term, the actual delineation of pore size can be challenging. It has been described as analogous to a room defined by walls and a door opening to it. In this case, the door is analogous to the pore throat, while the hydraulic radius of the pore throat defines the size of the pore, regardless of the shape of the pore (Ioannidis and Chatzis 1993). The pore size of samples and their distributions can be measured using a mercury porosimeter.

Assuming that the pores are cylindrical in shape, pore sizes could be calculated using the Washburn equation:

$$D = \frac{4\gamma \cos\theta}{P} \tag{8.3}$$

Where, $D$ is the pore diameter, $P$ is the pressure required to force the non-wetting liquid into a pore, $\gamma$ is the surface tension of intruding liquid, and $\theta$ is the angle of contact between the liquid and the sample. The pore size is related to an applied pressure to intrude mercury into the sample pores of radius $r$ or larger.

Pore size distribution is the table or graph of relative frequencies of pore sizes and is usually determined by fitting an experimental data to the Washburn's model (Dullien 1992). Pore size distribution is commonly determined with a mercury porosimeter (Karathanos, Kanellopoulos, and Belessiotis 1996; Kassama, Ngadi, and Raghavan 2003; Ngadi, Kassama, and Raghavan 2001; Rahman, Al-Amri, and Al-Bulushi 2002). The volume of mercury penetrating a sample is measured over a range of pressures. The pore size is calculated based on the capillary pressure obtained from the Laplace equation and using the bundle of capillary tubes (cylindrical) model of pore structure (Webb and Orr 1997). Pore size distribution influences textural characteristics of dried foods (Huang and Clayton 1990). Frying adjusts pore sizes and pore size distribution (Kassama, Ngadi, and Raghavan 2003; Ngadi, Kassama, and Raghavan 2001). The nature of the influence of frying on pore size and pore size distribution is yet to be clearly elucidated.

### 8.2.3 Factors that Influence Pore Structure

Heat and mass transfer parameters are related to the development of microstructure in deep-fat fried food products. Vapor pressure build-up during deep-fat frying exerts stress on the pore walls and deforms the pore structure within the porous medium. Other major factors that influence pore structure and development include composition of the food product, pretreatment and post-frying conditions.

The effect of temperature on moisture evaporation leading to pore development during frying is well documented (Gamble and Rice 1987; Hussain, Rahman, and Ng 2002; Kassama and Ngadi 2003; King, Lam, and Sandal 1968; Moreira, Castell-Perez, and Barrufet 1999; Pinthus and Saguy 1994). Elevated temperature increases the intensity of moisture migration from foods and consequently induces reorganization of pores. Although it is known that high frying temperatures changes pore structure in fried foods, how temperature specifically changes pore structure is not well known. New pores can be formed, whereas old pores can collapse during a heating process. This is the subject of ongoing research.

Pretreatment is another factor that influences pore structure formation. Different treatments have been applied to foods prior to frying to change their structure and control mass transfer during frying. These treatments include pre-drying, par-frying, microwave pre-cooking, and blanching. van Loon et al. (2007) pre-dried French fries before frying to reduce fat uptake and improve their texture. Other authors (Krokida et al. 2001c; Pedreschi and Moyano 2005) reported reduced oil uptake

in potato slices due to pre-drying. Pre-drying typically reduces the initial moisture content, as well as the number of open pores available in the product, resulting in reduced frying time and oil uptake. Similarly, par-frying should cause structural changes at the crust region of the food.

The composition of foods (especially moisture content) plays considerable part in pore development (Hussain, Rahman, and Ng 2002; Rahman, Al-Amri, and Al-Bulushi 2002). In particular, the initial moisture content largely determines the degree of pore developed. Mohamed, Hamid, and Hamid (1998) reported that an increase in initial moisture content of rice flour batter led to greater pore development and oil absorption when fried as a coating for foods.

Considerable progress has been made in the last decade on studies related to microstructure of foods and the effect of processing parameters (Aguilera 2005; Bouchon and Aguilera 2001; Bouchon, Aguilera, and Pyle 2003). Microstructural evaluations of fried food products tend to be largely quantitative due to the complexity of food structures. These make it difficult to evaluate the influence of pertinent process and product parameters quantitatively. More studies are required to advance knowledge in this regard.

## 8.3 QUALITY AS AFFECTED BY MICROSTRUCTURAL DEVELOPMENT IN FRIED FOODS

Quality can be understood as the consistent conformance of a product to the expectations of consumers. This is based on the characteristics and usability of the product. A wide range of indices, including texture, oil and moisture content, color, and flavor define the quality of fried products. Development of these quality indices are direct consequence of changes in microstructure as affected by product and process parameters. Some of the interactions between some quality indices and microstructure development have been alluded to in the previous sections of this chapter. Further discussion here will be on texture and color.

### 8.3.1 Texture

Texture refers to the group of physical characteristics of a food product that are sensed by sight, touch and mastication. These characteristics are related to the structural and mechanical attributes of the products. Texture can be assessed by sensory or instrumental techniques. The characteristics of the crust and the pore properties develop from the frying operation and account for textural properties. The crunchy texture of low-moisture fried products such as potato chips, tortilla chips, and corn chips can be attributed to the brittle, porous and honeycomb-like cell structure resulting from the puffing that occurs when water within the product vaporizes quickly and builds-up an internal pressure adequate to expand the matrix of the heat-softened solid. Similar microstructures are produced in hot-air puffing processes. The crunchiness of tortilla chips that were pretreated (steam drying and freeze drying) before frying was reported to increase with frying time (Kawas and Moreira 2001). Different pretreatments induced different degrees of starch gelatinization on the tortilla chips. The higher degree of gelatinization was impacted by steam drying. Thus, steam-dried

pretreated samples were softer, had a higher degree of puffiness, and higher porosity. On the other hand, pre-treating tortilla chips by freeze-drying resulted in the formation of a structure that allowed vapor to escape from the chips during frying, resulting in less puffing and less porosity after frying. These findings were confirmed with environmental electron scanning microscopy (ESEM) photomicrographs. Tortillas that were pretreated with freeze-drying showed more small pores that were close to each other, whereas steamed-baked pretreated tortillas had very large isolated pores. The freeze-dried pretreated chips were found to be crunchier than the steamed-baked chips, which was attributed to the smaller and more dispersed pore distribution in the freeze-dried pretreated samples. McDonough et al. (1993) also used ESEM, and observed that when baked tortilla chips were fried, moisture turned to steam and exited the chip, leaving behind a sponge-like network of small pores which became filled with oil. The texture/crispiness of the chips depended in part upon the particle size in the masa, the size of the pores, and the strength of the continuous phase after it became firm. Shyu, Hau, and Hwang (2005) reported an increase in crispiness of vacuum-fried carrot with increasing frying temperature and time. Pinthus, Weinberg, and Saguy (1995a) reported a positive correlation between texture and porosity in instrumental measurement of deep-fat fried restructured potato. Samples with high yield strength, indicating high crunchiness/crispiness, showed a relatively high porosity. Most microstructure–texture studies are on chips or potato fries, and less work has been reported for fried meat-based products. Llorca et al. (2001) studied the microstructure of fried battered squid rings. The authors observed that typical texture attributes such as sponginess and crunchiness were directly related to the release of water vapor during frying and the consolidation of structural elements of the product. The crust batter and the squid core layers remained intimately attached together in pre-fried samples, possibly because there was not enough time during the short pre-frying period (180°C for 30 s) to allow water vapor formed by heating to produce a separation of the two layers. However, in the final-fried product, cracks and pores were noticeable in the batter layer. Consolidation of structure was caused by gelatinization of starch granules in the batter coating and denaturation of proteins of the central sarcoplasm. Denaturation causes coagulation and contraction of fibers, which became more densely packed together as a result of interfibrillar water evaporation during frying. Llorca et al. (2005) examined the addition of hydrocolloids such as methylcellulose in batter and applied a pre-frying process of soaking battered squid rings in a hot water bath at 70°C followed by a short thermal treatment in a microwave oven. The pre-frying process allowed coagulation and denaturation in the batter coating before frying. Thus, a consolidated structure was formed by the pre-frying process and minimized the possibility of damage and resulting detachment of the batter coating from the core squid substrate before the frying. Addition of methylcellulose in the batter formulation produced a microstructural network that improved the batter coating and core interaction. Microstructure of batter-coated systems can also be modified by changing batter formulation ingredients, including type and state of flour used (Mukprasirt et al. 2001; Xue and Ngadi 2006; 2007). Protein denaturation and the resulting microstructural changes in batter-coated systems such as battered squid occur not only in the batter layer which is directly exposed to the frying oil, but also in the protein fraction of the core substrate (Llorca and

Hernando 2007). According to Miranda and Aguilera (2006), crispness arises when products with heterogenous pockets of air cells deform in a stepwise events of rise and sudden drop in the deforming force. Thus, crispness is associated with interparticle brittle fracture and the release of many small fragments of the product.

### 8.3.2 Color

Fried products undergo several color transitions during frying. Factors that affect the color of fried products include composition, surface properties, frying temperature and duration, and pretreatment process. For instance, it is known that the color of potato chips is related to the amount of reducing sugar content of the potatoes. Frying French fries at temperatures < 170°C was suggested to give acceptable light, less red and more yellow coloration (Krokida et al. 2001d). For chicken patties, frying at lower temperature (about 168°C) produced lighter patties compared with frying at higher temperature (about 190°C), which produced product with more redness (Yi and Chen 1987). Color changes in meats during heating can occur due to the oxidization and physical state of the pigment heme groups. Meat cooked by sous-vide treatment displayed more intense reddish color and less intense brownish-green color (Garcia-Segovia, Andres-Bello, and Martinez-Monzo 2007). This was attributed to reductions in deoxymyoglobin and oxymyoglobin, and an increase in metmyoglobin and sulfmyoglobin. Similar results were obtained for chicken meat (Liu and Chen 2001). Denaturation of colorless proteins (sarcoplasmic and myofibrillar) which usually occurs at 45–67°C, gives rise to opaque precipitates that tends to mask the still native red heme proteins hemoglobin, whereas at higher temperatures (67–79°C) denaturation of myoglobin and hemoglobin yields brown precipitates with significant effect on meat color (Martens, Stabursvik, and Martens 1982). Denaturation in meat samples can be observed by changes in optical reflectance/absorbance characteristics (Swatland 1989; 2006). By correlating optical signal changes in response to heating treatment, it is possible to monitor and assess meat quality changes during heating. Directly relating color changes with microstructural changes is complicated. However, it is well known that heating processes such as frying induce sequence of events such as protein denaturation, and starch gelatinization that change the color and structure of food sample.

## 8.4 TECHNIQUES FOR FOOD MICROSTRUCTURAL CHARACTERIZATION

Several techniques have being applied to study food microstructures. These include porosimetry, microscopy, X-ray, computed tomography (CT), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. Microscopy and X-ray methods provide visual images that can be studied subjectively and more precisely by the aid of computer software. These two techniques have been explored extensively in the study of food microstructures, while limited work has been done so far on fried foods. The various techniques have the potential to advance and contribute immensely to the way fried food qualities are studied, in novel food product development, and providing new tools for online quality assessment.

### 8.4.1 Porosimetry

Mercury intrusion porosimetry (MIP) has been used to characterize porosity, pore volume, pore area and pore size distribution in foods (Farkas and Singh 1991; Kassama and Ngadi 2005). Although, its use is not yet widespread in food studies, it is a common technique used for characterizing the structure of porous solids. Because mercury is a liquid that does not wet most solid surfaces, the size of the pore into which it can penetrate is inversely related to the applied pressure. MIP involves submerging a sample in mercury, applying pressure in steps, and recording the volumetric changes after each step. The principle of porosimetry is based on the relationship between intrusion and extrusion pressure (capillary pressure) and the pore dimensions of porous media. Assuming cylindrical pores, the Washburn equation (Equation 8.3) can be used to calculate pore dimension based on applied pressure (Giesche 2006).

Mercury has strong cohesive force and low or almost zero surface tension, which makes it resist wetting. Surface tension of mercury at 25°C is 484 dynes/cm and it shows high contact angle with solids, hence it is chosen in most porosimetry studies (Schoonman et al. 2001). The contact angle is usually between 130–140° for most food materials (Giesche, 2006; Mikijelj, Varela, and Whittemore 1991).

The pore size distribution is determined using the distribution function, $D_v(r)$, as defined by Adamson (1990):

$$D_v = -\frac{dV}{dr} = \frac{P_i}{r_i} \cdot \frac{dV}{dP} \tag{8.4}$$

where $dV$ is the volume of the intruded mercury in the sample (it is considered to be equal to the volume of pores), which is often determined numerically; $r$ is the pore radius ranging from $r_i$ to $r_i + dr$, and $P$ is the pressure changing from $P_i$ to $P_i + dP$. The pore distribution expression is based on the relation between pore radius and pore volume.

Experimental data provides volume of mercury intruded into the pores as a function of the applied pressure. Most porosimeters come with software that can be used to obtain $S$ and $D_v$ values. Characterization of pore structure using the MIP technique presents some challenges for fried foods. The technique is based on three assumptions: (1) pores are cylindrical; (2) wetting angle is constant throughout the microstructure; and (3) pore system remains undamaged during penetration. A non-cylindrical pore shape obviously has a different threshold pressure than that required for a cylindrical pore with an opening of the same size. In reality, a given threshold pressure must correlate to a range of pore sizes because pores are usually non-cylindrical and have various shapes. The wetting angle depends on the solid phase with which the mercury is in contact. Fried foods may contain solid, liquid and gas phases or otherwise may be dried to contain only solid and gas phases. Thus, a range of wetting angles must exist. A variation of 1° at a wetting angle of 130° results in an error of about 2% in the pore radius. The constant wetting angle assumptions may probably be sufficient for dried foods given the extremely large number of pores and the averaging effect inherent in the data. Pore damage and collapse of solid material at high intrusion pressure in complex pore-structure geometry could affect the accuracy of the MIP measurements. Mercury intrusion could be through all sides of the

sample, creating uniform volumetric pressure that could minimize structure damage. In an ideal situation, mercury intrudes a cylindrical pore when a sufficient pressure is reached and the recorded volume change during this intrusion is correlated with the corresponding pore size, giving a true measurement of the pore size and the volume associated with that pore size. Other pore shapes, such as a "bottleneck pore" (i.e., two pores separated by a smaller passage), give erroneous data. When the breakthrough pressure of a small pore in a bottleneck geometry is attained, the volume of the large pore intruded behind it is also measured. This underestimates the volume of the large pores and overestimates the volume of small pores. There may also be difficulty in measuring very small pore sizes because higher pressures are required to measure these sizes. Datta et al. (2007) used Galwick™ (chemical name Propene, 1,1,2,3,3,3-hexafluoro, oxidized, polymerized) to avoid some of the problems associated with mercury porosimetry. Galwick™ has a surface tension close to zero. Hot-air drying of samples before MIP measurements to remove liquid-phase species and minimize variations in wetting angle may result in not only shrinkage of the material, but also change the nature of a pore. This difficulty can be minimized by using freeze drying (Kassama and Ngadi 2005). It may be possible to compensate for the drying step required for MIP measurement for fried foods. Pore characteristics data may be adjusted based on certain assumptions such as complete displacement mechanism of mass transfer, minimal shrinkage of the samples, and zero initial porosity.

### 8.4.2 Microscopy and Food Imaging

Application of microscopy in food structural studies started in the early 20th century when light microscopes became an important tool in detecting adulteration in foods, which was a common occurrence. By the middle of the century, the application had progressed beyond detecting adulteration to studying structural properties of foods. Recent advances have helped to reduce production of artifacts, as well as to minimize or eliminate some of the tedious sample preparation steps associated with early microscopy.

Microscopy provides a means of visualizing structural and spatial configuration of food matrices at the macroscopic and microscopic levels. The scale covered range between $10^{-9}$ and $10^{-3}$ m. Microscopic techniques include optical/light microscopy (LM), confocal laser scanning microscopy (CLSM), electron microscopy (EM), atomic force microscopy (ATM). Some of these techniques allow non-invasive, real-time, three-dimensional rendering of images, and provides contrast between components for quantitative and qualitative assessment. Significant advances in computer-based image analysis have enhanced analysis of microscopic data.

LM is based on the transmission or reflection of visible light from a sample through a series of lenses to capture magnified images of an object on human eye(s), photographic plate, or on a digital screen. A simple optical microscope consists of two lenses: an objective and compound lens. The former is usually of small focal length, which magnifies the object, as real inverted image, within the focal length of the compound lens/eyepiece. The inverted image is further magnified by the compound lens to form a virtual image that is viewed at infinity. LM is in the category

of first-generation microscopes, which were widely used in medical and biological sciences before introduction into food study. The advantages of LM include observation of samples under different environmental conditions; selective staining to discriminate sample components; and ability to examine samples under different conditions, such as dried, frozen, wet and multiphase (Blonk and van Alast 1993).

Figure 8.8 compares the main components of electron microscopes and light microscope. Electron microscopes were developed to resolve the resolution limitations of LM. The systems use a guided electron beam to obtain images at a resolution that is two million times better than that possible by LM. The electrons are produced from three sources: field emission, lanthanum hexaboride and tungsten filament (Aguilera and Stanley 1999). The first two sources are preferred because they are low-energy sources, resulting in better resolution and improved brightness. However, tungsten filament is often used because of its simplicity and ease of operation. It has the highest melting point and the lowest vapor pressure of all the metals, allowing for ease of heating for electron production. Generated electrons are propagated in a vacuum environment to prevent collision with air constituents, which may cause electron deflection or scattering. A magnetic lens is used for focusing the beam on a sample. Types of electron microscope include transmission electron microscope (TEM), scanning electron microscope (SEM), and environmental scanning electron microscope (ESEM). In TEM, the electrons of the high-voltage beam form the image of the specimen whereas, in SEM, the images are produced by detecting low-energy secondary electrons which are emitted from the surface of the specimen due to excitation by the primary electron beam. In SEM, the electron beam is rastered across the sample, with detectors building up an image by mapping the detected signals with beam position.

The required tedious sample preparation protocols such as thin sectioning, fixation, drying, staining and embedding, place major limitations on EM for food

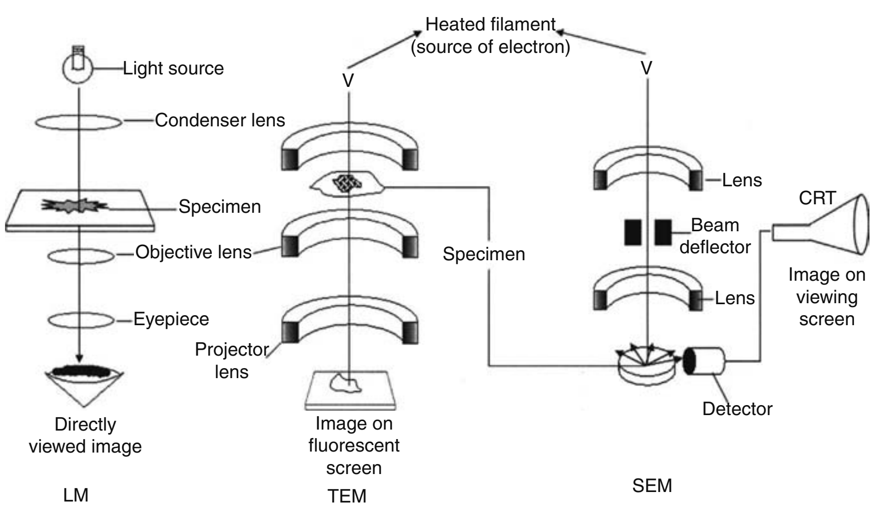



**FIGURE 8.8** Main components of a light microscope (LM), transmission electron microscope (TEM) and a scanning electron microscope (SEM).

applications. The development of ESEM has reduced some of these limitations, making it possible to scan samples under hydrated conditions. A capsule was recently developed for a new EM technique called WETSEM, to make imaging of wet materials, semi-liquids, oil and liquid materials under natural condition with minimal preparation possible (Quantomix 2006). The general limitation of microscopy techniques lies in the production of artefacts, which reduces details of information in images.

CLSM is a type of light microscopy with an enhanced ability to provide optical sectioning of sample instead of physical section and providing a means to eliminate out-of-focus images. CLSM operates by sequentially scanning the focal plane of the objective lens by a laser beam and collecting the fluorescence generated through a pin-hole detector (Figure 8.9). The pin-hole eliminates blurred images, providing an excellent resolution. An optical section of stained sample is obtained through point-by-point scanning of sample in the *x* and *y* coordinates in the focal plane. The movement of the focal point of the instrument through the depth of sample provides several two-dimensional images that are reconstructed in stack using an image analysis algorithm. CLSM is a powerful optical tool for visualizing structures of biopolymers mixtures like gels and emulsions, and food products generally (Blonk et al. 1995; Tromp et al. 2001).

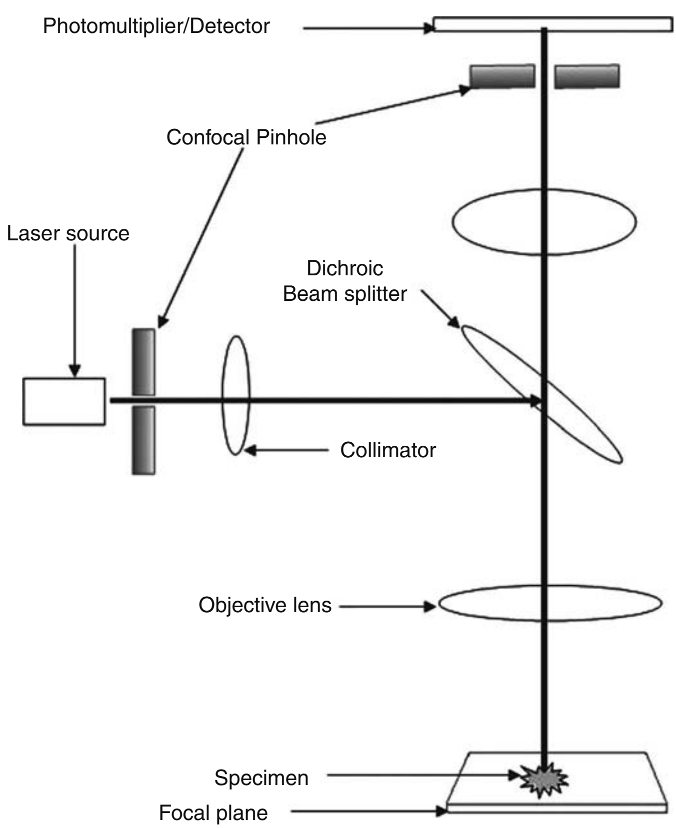



**FIGURE 8.9** A schematic diagram of confocal laser scanning microscope.

CLSM in food application is quite new and serves to solve some of the limitations posed by traditional LM and other methods, especially sample preparation, and the quality and type of image so produced, which often leads to artefacts (Kalab, Allan-Wojtas, and Miller 1995). It produces images from a single focal plane of sample with random thickness. The type of CLSM that is often used in food application produces contrast base on fluorescence emission from different components of the sample. The fluorescence could be autofluorescence or from staining sample with specific probes (van de Velde et al. 2003). When samples are stained with fluorescent dye, they spread base on accessibility and affinity. The use of multiple labeling is now a common approach to permit simultaneous assessment of several individual components in one sample. Staining could be covalently or non-covalently labeled, i.e., mixed or dropped on the sample. Among the stains that are used for staining biopolymers like carbohydrates (CHO) are fluorescein 5-isothiocynate (FITC) (CHO; protein), rhodamine B (protein) and Nile Blue/Nile red (fat) (Blonk and van Aalst 1993; van de Velde et al. 2003). CLSM requires minimal sample preparation, which involves cryo-sectioning at temperatures between –20°C and 30°C depending on the content.

### 8.4.3 X-Ray Computed Tomography (CT) Scanning

X-ray CT scanning is a method that was developed in the 1970s. It was primarily used in medicine to non-invasively scan the human body (Trater, Alavi, and Rizvi 2005). X-ray CT scanners have been classified into four categories based on their scale of resolution (Table 8.2). CT scanning techniques have been used successfully in medicine and material science to produce detailed internal morphology of human being, ceramics, metals, bone and granules (Farber, Tardos, and Michaels 2003; Olurin et al. 2002; Salvo et al. 2003). The most commonly used X-ray CT scanner in food application is the microtomography, which is also referred to as X-ray micro computed tomography (CT) (Lim and Barigou 2004; van Dalen et al. 2003) because of its smaller scale of operation. Its high resolving power to single-digit microns makes it a better tool for imaging intrinsic elements of heterogeneous systems such as food. It requires minimal or no sample preparation, it is non-invasive/non-destructive imaging; and provides three-dimensional rendition of images. These attributes make it a versatile tool in food imaging applications.

**TABLE 8.2**
**General Classification of CT Scanners Based on Resolution**

| CT Scanner Type | Scale of Observation | Scale of Resolution |
|---|---|---|
| Conventional | m | mm |
| High-resolution | dm | 100 μm |
| Ultra-high-resolution | cm | 10 μm |
| Microtomography | mm | μm |

Adapted from Ketcham and Carlson (2001).

To produce images, X-rays generated by an X-ray tube at very high energy in the range of 10–100 keV is focused on the sample. The X-ray beam transverses the sample, probing in at axial and lateral resolution up to the micrometers, capturing images at different angles. For more X-ray imaging, the sample is rotated at an angle perpendicular to the beam (Figure 8.10). Images are captured on sensitive X-ray camera, which produces an enlarged image in two dimensions, which are further processed by computer software by stacking together the two-dimensional images to form a three-dimensional image.

Contrast is produced based on density of sample, which also determines the amount of absorbed X-ray energy. This is quantified as the CT number. For example, the CT number of air and water are –1000 and 0, respectively (Tollner et al. 1989). CT number is related to the density of the material by the following expression (Kim et al. 2007):

$$\rho = 1 + \frac{CT}{1000} \tag{8.5}$$

X-ray CT has been used non-invasively to distinguish changes during ripening of peaches, which has potential in robotic harvesting of peach and sorting based on maturity (Barcelon, Tojo, and Watanabe 1999). Lim and Barigou (2004) used X-ray micro CT to study the microstructure of a number of cellular food products, acquiring useful quantitative data about the cell network, cell distribution and extent of anisotropy of microstructure. Miri et al. (2006) established the enormous potential of using X-ray micro CT to study complex food systems such as deep-fat fried foods microstructures. Adedeji and Ngadi (2007) also presented application of X-ray micro CT for fried food coating. The technique was used to study in details the microstructural characteristics of chicken nuggets coating (Figure 8.11).

### 8.4.4 Image Analysis

Qualitative and quantitative analysis of images acquired in the various techniques is done with various types of software on computer platforms that are very versatile. The human eye is incapable of objective and quantitative determinations of the image features observed under the microscope. Computer technology and

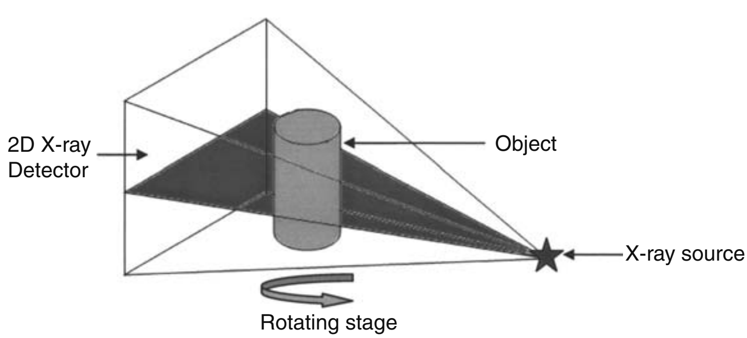



**FIGURE 8.10** X-ray system (schematic).

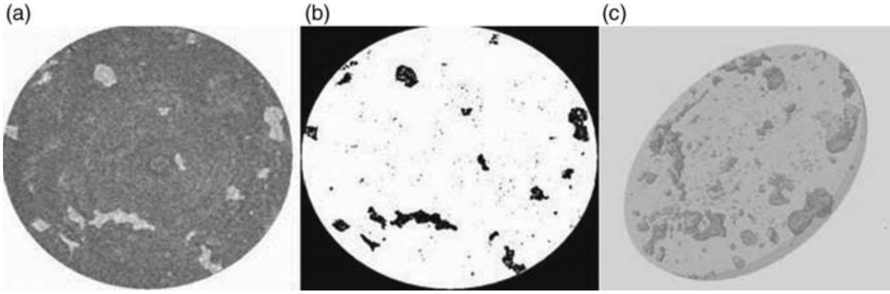



**FIGURE 8.11** Scanned images of two-dimensional slice of breading coating of fried chicken nuggets (180°C for 4 min) (a), the binarized form (b), and three-dimensional reconstructed image (c).

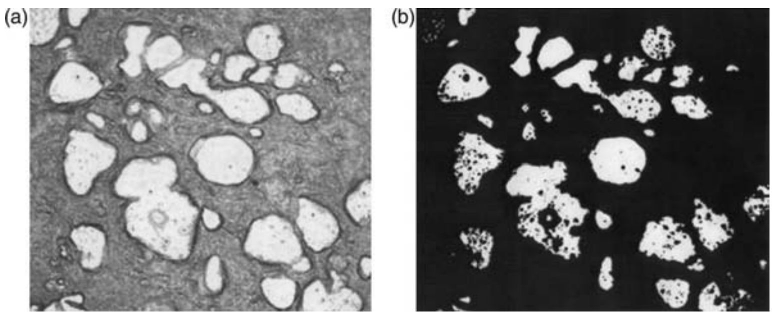



**FIGURE 8.12** Chicken nuggets breading coating micrograph obtained from light microscope (LM) (a) and Binarized image from LM micrograph (b) obtained using ImageJ software from National Institute of Health, USA.

mathematics have played a great part in recognizing, differentiating, editing and quantifying images. Some of the technologies can perform segmentation on grayscale and color images. There are a number of software packages that have been developed for image processing which have wide application, from biology to material science and food systems. Differentiation and quantification of components of foods such as pores and the food matrix that supports it, protein body and carbohydrates is possible by separation methods of thresholding and binarization. Some of these software packages have the capability for stereological studies, that is, the production of three-dimensional images from set of successive two-dimensional images using the mathematical procedure of interpolation between the preceding slides.

A very important step in quantitative analysis of image components in grayscale is segmentation. This is a step in which the object/region (e.g., pores) of importance is separated from the rest of the system through a process of binarization by setting a threshold level for black and white. The object could be in either of the colors. For the example shown in Figure 8.12 of LM micrographs of chicken nuggets breading coating, the pores take the white color while the rest of the food is black and in the background. The segmented/binarized image is then analyzed to obtain quantitative

information such as pore count, diameter and area distribution, which can be outputted in numerical form or graphically as histograms.

## 8.5 CONCLUSIONS

The future of fried foods impinges on better understanding of various changes taking place at the microstructural level and their correlation with quality characteristics. It is evident that more studies need to be carried out. The introduction of advanced imaging techniques from other sciences holds so much promise because they provide invaluable tools for food microstructural study. The protocols for application of some of these techniques are still being evaluated, but their potential is enormous.

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# 9 Flavor Changes During Frying

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## CONTENTS



## 9.1 INTRODUCTION

Deep-fat frying is a popular method of food preparation because it imparts a desirable deep-fried flavor that is not developed during other cooking methods such as baking. Understanding how flavors are developed in oils during the frying process is important to know to enhance positive flavors and inhibit negative flavors. Briefly, flavors in frying oils can be from one or more of the following: naturally occurring flavors (e.g., peanut oil and olive oil); flavors imparted from processing procedures (e.g., hydrogenation); and degradation of fatty acids at the high temperatures used in frying. Development of flavors from the decomposition of fatty acids is the most significant of these three effects, and is the primary focus of this chapter. In addition, the chemistry of frying will be briefly discussed because it relates to flavor development during frying.

## 9.2 PHASES OF THE FRYING PROCESS

Oil goes through approximately five phases as it is used for frying unless conditions are controlled to keep the oil in a state of equilibrium. In the first phase of the frying cycle, the oil is fresh, so oil during this time provides only a small amount of browning and food may look undercooked. Deep-fried flavor intensity of the food is usually also low because little oxidation has occurred. Frying operators often heat or fry in a fresh oil for a few hours to condition the oil. The fried food may or may not be discarded. In the second phase of the cycle, the oil is at its optimum. Food has a desirable golden-brown color; is fully cooked; and has optimal deep-fried flavor. The low amount of oil oxidation that has occurred by this time is needed to provide the desirable deep-fried flavor in the food. Some oils will develop this characteristic deep-fried flavor more quickly than others depending on the linoleic acid content of the oil. This aspect will be discussed more extensively later in the chapter. During the third phase, the oil continues to deteriorate because of hydrolysis, oxidation and polymerization, leaving the oil lower in quality than at the second phase, but oil quality is still acceptable. Fried food at this phase will have a darker brown color and slight off-flavors may be detectable in the food. By the fourth phase, the oil has deteriorated even further and oil quality is marginal. Food has a dark-brown color and moderate-to-strong off-flavors; and the oil will probably foam. Foaming prevents uniform cooking of the food, so the fried food may not be fully cooked. By the time the oil reaches the fifth and final phase of its fry life, severe oil degradation has occurred. Foaming of the oil is a major problem, and fried food has unacceptable flavors and may not be fully cooked in the center because foaming of the oil has limited direct contact of oil and food. Unless frying conditions are adjusted to maintain the oil in the second phase of the cycle, the oil will continue to deteriorate and may have to be discarded.

## 9.3 CAUSES OF FRYING OIL DETERIORATION

Degradation of frying oil is affected by many factors, such as unsaturation of fatty acids, oil temperature, oxygen absorption, metals in the food and in the oil, and type of food. Addition of foods to the frying oil lowers oil stability because of the increased oxygen from this process. Intermittent and continuous frying significantly affects fry life. For example, cottonseed oil intermittently heated had as much polar material as oil heated continuously for three times' longer (Perkins and Van Akkeren 1965). This difference may have been caused by increased amounts of fatty acyl peroxides that decomposed upon repeated heating and cooling, causing further oil damage. Replenishing the fryer with fresh oil is common in most frying operations. However, in the snack food industry, where more make-up oil is added than in restaurant frying, a complete turnover time of 8–12 hours can be achieved in a continuous fryer. Other factors that affect the amount of oil deterioration during frying include initial oil quality, degradation products in the oil, and additives to the oils (e.g., antioxidants and anti-foam agents). Frying time and rate, fryer type, surface-to-volume ratio of the oil, addition of makeup oil, and filtering of oil also affect oil deterioration.

## 9.4 CHEMICAL CHANGES DURING FRYING

The chemical reactions in frying are discussed in chapter 3 and chapter 4, but a brief review is necessary to relate these processes to flavor changes that can occur. During frying, hydrolysis, polymerization and thermal oxidation take place and affect the flavor of the oil and the fried food positively and negatively. The main objective of frying is to produce a distinctive deep-fried flavor and crisp texture. A few chemical changes are necessary so food will have a golden-brown color and deep-fried flavor. Oil that has just reached frying temperature will not produce the color and flavor typical of oil that has been conditioned or heated for several hours before frying. During deep-fat frying, oils decompose to form volatile products and non-volatile monomeric and polymeric compounds (Figure 9.1). The increases and decreases in these compounds and also the variation of physical properties of oil during frying given in Figure 9.1 are approximations, and vary depending on oil composition and frying conditions described in later sections of this chapter. Chemical changes during frying increase peroxides, volatile compounds, free fatty acids, polar materials and polymeric compounds. With continued heating and frying, peroxides and volatile compounds further decompose until breakdown products accumulate to levels that produce off-flavors. The amounts of these compounds that are formed and their chemical structures depend on many factors, including oil composition and food types, frying conditions and oxygen availability. Hydrolysis, oxidation, and polymerization are interrelated and produce a complex mixture of products.

### 9.4.1 OXIDATION

Oxidation has a major effect on oil flavor in frying. Oxygen and heat produce a series of reactions in oil, including formation of free radicals, hydroperoxides and conjugated dienes in the early phase. Further chemical reactions occur during the oxidation

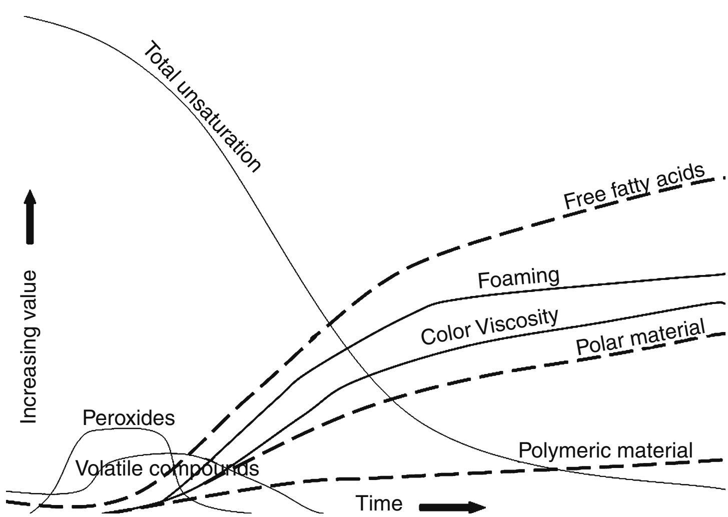



**FIGURE 9.1** Approximation for the variation of products formed in oil, and the physical properties of oil during frying.

process to produce volatile and non-volatile decomposition products. The oxidation mechanism in frying oils is similar to autoxidation at room temperature; however, the unstable primary oxidation products (hydroperoxides) decompose rapidly at frying temperatures into secondary oxidation products, such as aldehydes and ketones (Figure 9.2). Secondary oxidation products are volatile, and contribute significantly to the flavor of the oil and fried food. For example, unsaturated aldehydes such as 2,4-decadienal, 2,4-nonadienal, 2,4-octadienal, 2-heptenal, or 2-octenal decompose from the breakdown of linoleic acid and contribute to the desirable, deep-fried flavor in oils during the second phase of the frying cycle (Warner et al. 2001). However, saturated and unsaturated aldehydes such as hexanal, heptanal, octanal, nonanal, 2-decenal produce distinctive off-odors in frying oil. The fruity and plastic off-odors typical of heated high oleic oils can be attributed primarily to heptanal, octanal, nonanal, 2-decenal and 2-undecenal (Neff, Warner, and Byrdwell 2000). In deteriorated frying oil, acrolein is primarily responsible for the typical acrid odor. Analysis of primary oxidation products, such as hydroperoxides, by methods such as peroxide value at any one point in the frying process provides little information because their formation and decomposition change rapidly, as can be partially seen from Figure 9.1. During frying, oils with polyunsaturated fatty acids, such as linoleic acid, have a distinct induction period of hydroperoxide formation followed by a rapid increase in peroxide values, then a rapid destruction of peroxides. Oxidative degradation will produce oxidized triacylglycerols containing hydroperoxide-, epoxy-, hydroxy-, and keto-groups and dimeric fatty acids or dimeric triacylglycerols. Volatile degradation products can be saturated and monounsaturated hydroxy-, aldehydic-, keto-, and dicarboxylic-acids; hydrocarbons; alcohols; aldehydes; ketones; and aromatic compounds.

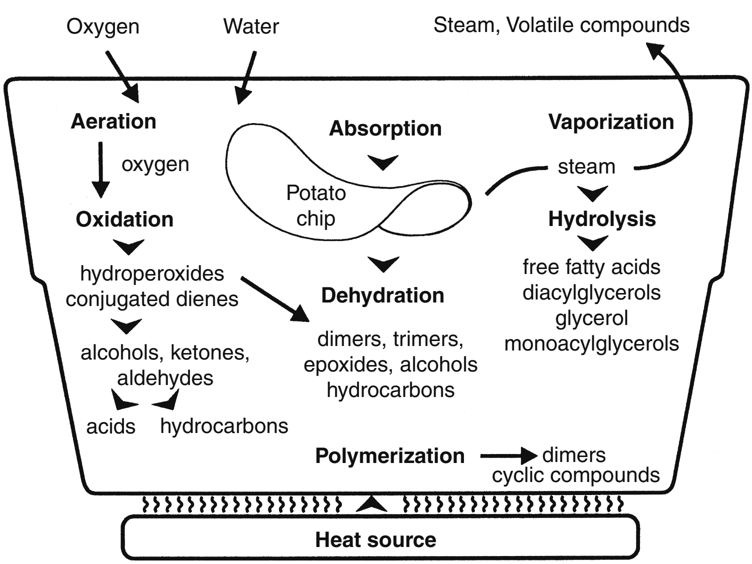



**FIGURE 9.2** Physical and chemical reactions in the fryer.

### 9.4.2 Polymerization

Polymerization forms compounds with high molecular weight and polarity that can form from free radicals or triacylglycerols by the Diels–Alder reaction. Cyclic fatty acids can form within one fatty acid; dimeric fatty acids can form between two fatty acids, either within or between triglycerides; and polymers with high molecular weight are obtained as these molecules crosslink. The viscosity of the oil increases as polymerized products increase in the frying oil (Figure 9.1). The compounds formed by polymerization can serve as precursors for off-flavors. Therefore, deteriorated oil will probably have increased amounts of off-flavors, such as acrid and burnt, and the fried food also develops off-flavors.

### 9.4.3 Hydrolysis

Hydrolysis produces monoacylglycerols, diacylglycerols, and free fatty acids (Figure 9.1). Degradation products from hydrolysis decrease the fry life of the oil. The level of free fatty acids can be used to measure the degree of hydrolysis in the oil.

## 9.5 COMPOUNDS FORMED BY OIL DEGRADATION

In deep-fat frying, thermal and oxidative decomposition of the oil occur, producing volatile and non-volatile decomposition products. These two types of compounds are important because the volatile compounds affect the flavor of the food, whereas the non-volatile compounds affect the fry life of the oil and the shelf-life of the fried food. The non-volatile compounds can also serve as precursors to further oil deterioration. Volatile compounds are primarily responsible for the positive and negative flavors in the fried food. Undesirable off-flavors can be produced if frying oil is allowed to deteriorate. Non-volatile compounds, such as polymers, at low levels, may not have much effect on the flavor of a food that is consumed immediately after frying; however, they affect the fry life of the oil and the shelf-life of aged fried food. Monomers formed may include conjugated dienes, cyclic monomers, and free fatty acids; whereas polymers may be non-polar, polar, or cyclic (5- or 6-membered rings). Non-volatile products in deteriorated frying oils include polymeric triacylglycerols, oxidized triacylglycerol derivatives, and cyclic compounds. Polymeric triacylglycerols result from condensation of two or more triacylglycerol molecules to form polar and non-polar high molecular weight compounds. The non-polymerized part of the oil contains mainly unchanged triacylglycerols in combination with their oxidized derivatives. In addition, it contains monoacylglycerols and diacylglycerols, partial glycerides containing chain scission products, triacylglycerols with cyclic and/or dimeric fatty acids, and any other non-volatile product. However, much oil deterioration is needed for a significant amount of these polymers to form. In continuous snack food processing, such as potato chips, this is not usually a problem because frying conditions are carefully monitored and a high oil turnover rate is achieved to reach equilibrium. However, oil used in industrial batch fryers (kettle fryers) or small-scale batch frying operations, such as restaurants, oil usually deteriorates more.

When oils are heated to frying temperatures, many compounds are produced as the fatty acids degrade. For example, pentane, acrolein, pentanal, 1-pentanal,

hexanal, 2- and/or 3 hexanal, 2-heptenal, 2-octenal, 2, 4-nonadienal, 2, 4-octadienal, and 2, 4-decadienal are formed from linoleic acid. These compounds produce characteristic odors and flavors that affect the flavor of the frying oil and fried food. Most of the volatile compounds (aldehydes, ketones, alcohols, acids, esters, hydrocarbons, lactones, furans) are in general undesirable, except for 2,4-decadienal, which is known to be the major contributor to deep-fried flavor, but 2-heptenal, 2-octenal, 2,4-nonadienal, 2,4-nonadienal, and 2,4-octadienal also are described as producing a deep-fried odor (Warner et al. 2001). Most of the degradation products produce off-flavors. For example, acrid flavor is a result of acrolein from the decomposition of acid. Volatile compounds from the oxidation of oleic acid produce undesirable fruity and plastic/waxy flavors. Heptane, octane, heptanal, octanal, nonanal, 2-decenal, and 2-undecenal can be found in high oleic oils because they form from the oxidation of oleic acid. Linolenic acid degradation produces volatile compounds such as propanal and 2-hexenal and a fishy flavor in the oil and fried food.

## 9.6 MEASURING DETERIORATION PRODUCTS RELATED TO FLAVOR

Many of the volatile decomposition products formed during frying volatilize and/or further decompose, so it is difficult to get an accurate measure of oil deterioration by instrumental and chemical analyses of these compounds. Methods that measure volatile compounds directly or indirectly include gas chromatographic volatile compound analysis and sensory analysis. These methods are better for measuring the quality and stability of the fresh and aged fried food than for measuring the quality of the frying oil. Peroxide value is not a good measure of deterioration in frying oils because peroxides are unstable at frying temperature. Peroxides decompose very easily into secondary oxidation products, so analysis of peroxides at random times of oil use provides little information about the overall quality of the oil. Gas chromatographic volatile compound analysis measures compounds that are directly related to the flavor of the fried food. Identifying volatile compounds in fried food is important because these compounds help in understanding the chemical reactions that occur during frying, and because the flavor of deep fried food is caused by the volatile compounds. Although the volatile compounds in the frying oil are continually changing, measuring these compounds in the frying oil can give some indication of oil deterioration, but care should be taken in interpreting data on volatile compounds in used frying oil because of the fluctuations in formation and degradation of the compounds at frying temperature. Gas chromatography–mass spectrometry (GC/MS) can be used to identify volatile compounds in frying oils, such as hydrocarbons, aldehydes, alcohols, furans, esters, ethers, acids and lactones. Volatile compounds can be identified and quantified from fresh and aged fried food more reliably than in the frying oil. Sensory evaluation of fried food is a good method to determine when to discard frying oil. Scientific groups in Germany use sensory assessment of frying oils; however, if assessment does not give a clear indication that the oil is deteriorated, instrumental or chemical analysis is used to support a final decision on oil quality. The Third International Symposium on Deep-Fat Frying recommended that sensory parameters of the fried food be the principal quality index for deep

fat frying. To further confirm oil abuse, total polar materials should be < 24% and polymeric triacylglycerols < 12% (Anonymous 2000). Sensory analysis of frying oil and fried-food quality may be conducted by analytical descriptive/discriminative panels using trained, experienced panelists or by consumer panels using untrained judges. However, results from consumer panels that measure the flavor likeability of food are usually dependent upon individual likes and dislikes, rather than objective standards used by trained panels. Consumer panels may find no differences in fried food flavors, whereas a trained, experienced analytical descriptive panel can usually detect significant differences in the type and intensity of flavors in fried food prepared in various oil types.

## 9.7 SOURCES OF FLAVORS IN FRYING OILS

As stated in the introduction, there are three major sources of flavor in frying oils. First, naturally occurring flavor compounds in oils give distinct flavors to all oils. These distinct flavors are most noticeable after the oil is extracted or expelled from the oilseed. Many oils are refined and deodorized to remove all or most of these flavor compounds in oils such as soybean, canola (low erucic acid rapeseed) and sunflower. Other oils such as olive oil are pressed without further processing so the natural flavor of the oil is evident. On the other hand, some oils such as corn and peanut are processed to leave some of the natural positive flavors in the oil. In some countries, such as the USA, peanut oil is used for fried snack foods because of its unique and desirable nutty flavor. Processing of oil can also affect frying oil flavor. For example, when oil is hydrogenated, it develops a specific flavor that is often described as fruity, flowery, and/or milky. The greater the degree of hydrogenation, the more distinct this flavor becomes. Finally, the primary source of flavor in frying oils comes from the decomposition of the major fatty acids, oleic, linoleic, and linolenic at temperatures of approximately 180°C, which will be discussed in more detail later.

## 9.8 FLAVORS FROM DECOMPOSITION OF FATTY ACIDS

In his book on lipid oxidation, Frankel (2005) outlined the relative reactivity to oxygen for the major fatty acids. If the reactivity to oxygen is set at 1 for oleic acid, then linoleic acid is 50 times more reactive than oleic acid and linolenic acid is 100 times more reactive than oleic acid (Table 9.1). If we extrapolate these values to frying oil, oil with high amounts of linolenic acid such as canola (low erucic acid rapeseed)

**TABLE 9.1**
**Relative Rates of Reactivity of Fatty Acids with Oxygen**

| Fatty Acids | Relative Rates of Reactivity with Oxygen |
|---|---|
| Oleic (C18:1) | 1 |
| Linoleic (C18:2) | 50 |
| Linolenic (C18:3) | 100 |

with 10%, will oxidize rapidly during frying and develop off-flavors or negative flavors, such as fishy from linolenic acid decomposition that are not acceptable in frying oils and fried foods. Therefore, canola (low erucic acid rapeseed) and soybean are not generally used for commercial frying because the three double bonds found in these oils are easily oxidized. On the other hand, an oil with high amounts of oleic acid ( $>$ 70%) will not oxidize rapidly. When oleic acid oxidizes, it forms compounds such as heptane, octane, heptanal, octanal, nonanal, 2-decenal, and 2-undecenal that are described as waxy, fruity and plastic. As stated previously, the desire for the delicious deep-fried flavor is one of the main reasons that we consume fried food. The deep-fried flavor is produced from some of the volatile compounds formed from the oxidation of linoleic acid. Cottonseed oil with its high (52%) level of linoleic acid is considered a good frying oil because of the desirable deep-fried flavor it produces. Therefore, a small amount of oxidation in the fryer oil is a positive attribute as in the case of linoleic acid decomposition, which produces 2,4-decadienal as one of its major degradation products. However, greater amounts of oxidation of linoleic acid can produce off-flavors.

Some fatty acid composition profiles can cause unique flavor profiles in frying oils. For example, high oleic soybean oil with 85% oleic acid has more linolenic acid than linoleic acid (Table 9.2). In flavor analysis of potato chips fried in cottonseed oil, high oleic soybean oil, low linolenic acid soybean oil or a 1:1 blend of the high oleic and low linolenic oils, the chips fried in the high oleic oil had a significantly higher fishy flavor intensity than any of the other chips for the most of the storage testing (Figure 9.3) (Warner and Gupta 2005). This unusual flavor situation was unexpected because of the low amount of linolenic acid in the high oleic oil (2.3%). However, the fishy flavor was noticeable probably because few oxidation products were formed from the low level of linoleic acid (1.3%) and because the oleic acid does not oxidize easily. If the linoleic acid content were higher, its oxidation products could probably help to mask flavors from linolenic acid and the fishy flavor could be less detectable.

## 9.9 DETERMINING SOURCES OF FLAVORS IN FRYING OILS

Warner, Orr, and Glynn (1997) showed that high oleic acid oils that had low amounts of linoleic acid produced fried food with low intensities of deep-fried flavor. If the potato chips fried in high oleic sunflower oil, cottonseed oil or blends

**TABLE 9.2**
**Fatty Acid Compositions of Soybean Oils**

| Fatty acids | Soybean oil (standard) | Low linolenic soybean oil (LL) | High oleic soybean oil (HO) | 1:1 blend of HO:LL |
|---|---|---|---|---|
| C16:0 | 9.7 | 10.8 | 7.3 | 8.9 |
| C18:0 | 3.5 | 4.5 | 3.4 | 3.9 |
| C18:1 | 25.2 | 26.1 | 85.0 | 54.0 |
| C18:2 | 54.2 | 55.4 | 1.3 | 31.0 |
| C18:3 | 6.4 | 3.0 | 2.3 | 2.1 |

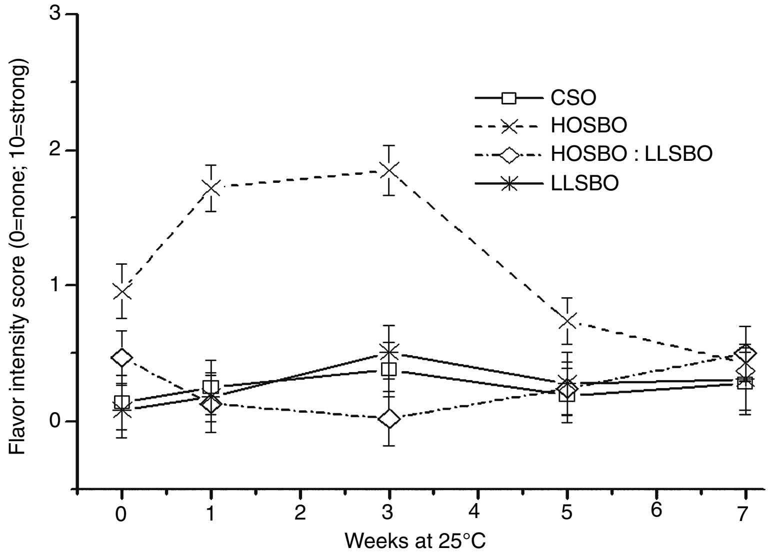



**FIGURE 9.3** Intensities of fishy flavor in potato chips fried in soybean oil (SBO), low linolenic acid SBO, high oleic acid SBO, and 1:1 LLSBO and HOSBO and aged up to 7 weeks at 25°C.

of these two oils were compared, potato chips had the highest intensity of deep-fried flavor when fried in cottonseed oil, and the lowest when high oleic sunflower oil was used. Furthermore, studies were conducted to determine sources of the desirable deep-fried flavor in heated oils and fried foods. Triolein and trilinolein were heated at 190°C and with added water to partially simulate frying (Neff, Warner, and Byrdwell 2000; Warner et al. 2001). Samples were heated until polar compounds ranged from 5 to 31% representing low, moderate and high amounts of lipid degradation. Volatile compounds were measured by purge and trap gas chromatography-mass spectrometry-olfactometry. 2,4-Octadienal, 2,4-nonadienal and 2,4-decadienal produced a deep-fried odor at moderate-to-strong intensity levels in the heated trilinolein as determined by olfactometry. Data for 2,4-decadienal produced by trilinolein and triolein is shown in Figure 9.4. The small amount of 2, 4-decadienal found in heated triolein shows why little deep-fried flavor is detected in foods fried in high oleic/low linoleic acid oils. The 2-alkenals, including 2-heptenal and 2-octenal, produced deep-fried odors in heated trilinolein. The same aldehydes were also found in triolein heated for 6 h (31% polar compounds) but in low amounts, and the olfactometry intensity levels for deep fried were low. Reversed-phase high-performance liquid chromatography (HPLC) coupled with atmospheric pressure chemical ionization mass spectrometry of the fractionated triolein and trilinolein showed variation in the production of the volatile precursors from epoxy, keto and dimer oxidation products. These decomposition products represent molecular markers for the pathways of the 2-alkenals and 2, 4-alkadienals in triolein and trilinolein. For triolein, 2,4-nonadienal, 2,4-decadienal, and 2,4-undecadienal can be cleavage products of the 6,7-; 7,8-; 9,10-; and 11,12-epoxy

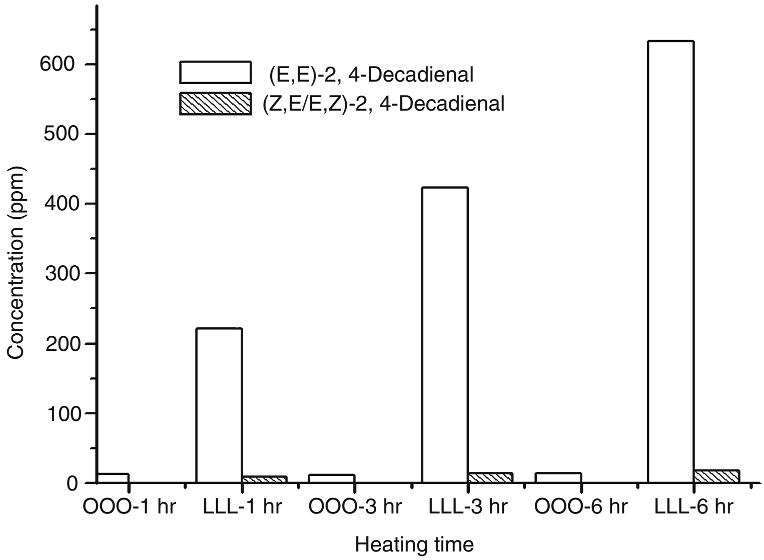



**FIGURE 9.4** Amounts of 2,4-decadienal in triolein (OOO) and trilinolein (LLL) heated at 190°C for 1, 3, or 6 hr.

trioleins, respectively. In heated triolein, the predominant odors were fruity and plastic. Some of the volatile compounds that produced negative odors were heptanal (fruity), octanal (fruity), (Z)-2-decenal (plastic) and (E)-2-decenal (plastic) and 2-undecenal (plastic). Figure 9.5 shows the amounts of 2-decenal and 2-undecenal in heated triolein. Neither of these compounds was found in heated trilinolein.

## 9.10 CONTROLLING FLAVOR DEVELOPMENT IN FRYING OILS

The general factors that help inhibit frying oil deterioration include choosing fresh oil with good initial quality that has no prior oxidation and low amounts of catalyzing metals. The extent of the degradation reactions of hydrolysis, polymerization and oxidation can be controlled by carefully managing frying conditions, such as temperature and time, exposure of oil to oxygen, continuous frying, oil filtration, turnover of oil, and addition of citric acid, antioxidants and/or anti-foam agents.

As discussed previously, the fatty acid composition of the frying oil has a major effect on the flavors in the oil and fried food. Therefore, modifying the fatty acid composition will help to control the flavor development in the oil. Hydrogenation, one of the first tools that oil processors used to control flavor development in frying oils, increased oleic acid and decreased linoleic acid and linolenic acid. However, hydrogenation produces *trans* fatty acids that are not healthful, and it also contributes a distinct flavor that is not acceptable to some food manufacturers. Plant breeding for specific fatty acid compositions is another alternative to control flavor in oils. Since the mid-1980s, plant geneticists have been modifying fatty acid compositions by plant breeding techniques. Based on over 50 years of edible oil

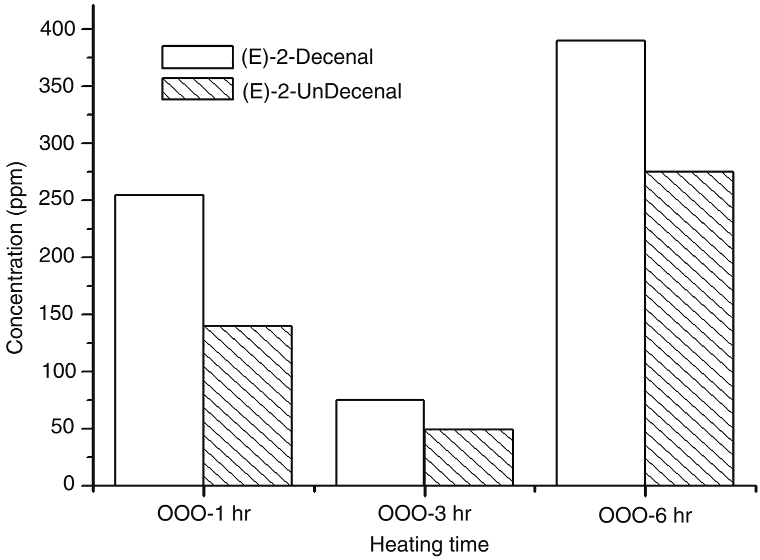



**FIGURE 9.5** Amounts of 2-decenal and 2-undecenal formed in triolein (OOO) heated at 190°C for 1, 3, or 6 hr.

stability research, the targets for modifying fatty acid compositions of oilseeds by plant breeding were identified as lower linolenic acid, lower linoleic acid and higher oleic acid. The research on oils with reduced linolenic acid was an early objective and resulted in liquid salad oils with increased oxidative stability (Liu and White 1992a; Miller and White 1992; Mounts et al. 1988). In other reports, oils with high amounts oleic acid and/or lower levels of linolenic acid had improved stability to degradation during the frying compared to their unmodified counterparts of sunflower, corn, soybean, and canola (low erucic acid rapeseed) oils (Eskin et al. 1989; Liu and White 1992b; Mounts et al. 1994; Warner and Knowlton 1997; Warner and Mounts 1993). However, frying studies that included chemical and sensory analyses of the fried food and oils determined that as the amount of oleic acid was increased with corresponding decreases in the amount of linoleic acid, the quality and intensity of the deep-fried flavor of the fried food decreased (Warner and Knowlton 1997; Warner and Mounts 1993; Warner, Orr, and Glynn 1997; Warner et al. 1994). In addition, these high oleic acid oils also produced increased intensity levels of undesirable aromas such as fruity, plastic, acrid, and waxy at high temperatures. Frying operators can optimize the flavor development in their frying oils and fried food by the fatty acid compositions they select. For example, Cargill, a major oil producer in the USA market, produces two types of high oleic/low linolenic acid canola oils. One of these oils, “Clear Valley 75”, has 75% oleic acid and 12% linoleic acid, and is sold for high-stability uses and is described as delivering a neutral flavor. On the other hand, “Clear Valley 65” has 65% oleic acid and 22% linoleic acid, and is described as providing superior stability and improved fried flavor in the food.

## 9.11 RECOMMENDATIONS FOR GOOD FLAVOR AND GOOD STABILITY IN FRYING OILS/FRIED FOOD

The amount and type of degradation products formed in frying oils is primarily dependent on the fatty acid composition of the frying oil, so it is important to keep this in mind in selecting frying oils. Even though linolenic acid is a healthful fatty acid, it is also very oxidizable, as previously discussed. Therefore, reducing linolenic acid to $< 3\%$ is necessary for good oil stability and for limiting development of off-flavor. In addition, linoleic acid should be present in the oil in greater amounts than the linolenic acid to not only provide for good deep-fried flavor, but also to help mask off-flavors from the linolenic acid degradation. Even though linoleic acid oxidizes in the fryer, some is needed for developing a deep-fried flavor. Therefore, linoleic acid should be in the 20–30% range (Warner, Orr, and Glynn 1997). The precise level can be adjusted to meet the fry life requirements of the oil and the shelf-life needed for any stored fried food. In general, most of the modified composition oils have the following characteristics. Low linolenic acid containing oils give only moderate frying stability, but they have high deep-fried flavor intensity because the linoleic acid content can still be high at 50–55% as in soybean oil. High oleic oils give good frying stability and high waxy/plastic flavor intensity from oleic acid decomposition, but they are low in linoleic acid, so they have low deep-fried flavor intensity. Finally, mid-oleic oils have 50–70% oleic acid for high frying stability and 20–30% linoleic acid for high deep-fried flavor intensity. It is possible to get good deep-fried flavor and good stability in frying oils and fried foods.

## 9.12 CONCLUSIONS

The sources of flavors in frying oils come primarily from natural compounds, processing, and/or degradation of fatty acids. High oleic oils limit intensity of deep-fried flavor because they contain low amounts of linoleic acid. A low level of oxidation in the fryer oil is important for developing deep-fried flavor from linoleic acid; however, too much oxidation of linoleic acid produces off-flavors, such as acrid flavor. Extremes in fatty acid composition, e.g., very high or very low levels of fatty acids, for frying oils are not generally necessary. However, linolenic acid should be at low amounts of $\leq 3\%$ to minimize off-flavors from the rapid decomposition of this fatty acid. A wide variety of regular vegetable oils and ones with modified fatty acid compositions are available for food manufacturers and frying operators to be able to optimize the fatty acid compositions of their oils to ensure good flavor development and stability of their oils and fried foods.

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# 10 Rheology of Batters Used in Frying

*Teresa Sanz and Ana Salvador*

## CONTENTS

## 10.1 INTRODUCTION

The rheological properties of batters for frying have a decisive influence in determining the final quality of battered food. Batter rheology may be more accurate than any other property in predicting final battered food quality. Apart from being a determining factor for correct batter machinery performance, batter rheology directly or indirectly determines very important battered food quality attributes such as pick-up, adhesion, appearance and texture, as well as final moisture and oil content. Batter ingredients bear the main responsibility for the rheological properties of the batter. Knowledge of the specific contribution of batter ingredients to the rheological properties of the battered food, as well as to its final quality, is essential for satisfying a specific necessity.

This chapter reviews the importance of rheology for the different steps of the battered manufacturing process and its relationship with final battered food quality. The contribution of the most commonly employed batter ingredients is also discussed. In addition, a basic introduction to the science of rheology and how to measure the rheological properties of batters is also given.

## 10.2 DEFINITION OF RHEOLOGY: BASIC CONCEPTS

Rheology is the branch of physics that studies the deformation and flow brought about in materials by the action of mechanical forces (Everett 1992).

From the rheological view point, the basic behavior patterns of substances are known as "elastic behavior" and "viscous behavior".

Elastic behavior is a characteristic of solids which are deformed under the influence of "small" external forces so that when the forces are removed, the deformation is spontaneously reversed. In the simplest cases, the rheological properties of these materials can be described by Hooke's law, which states that the force applied (stress) is directly proportional to the deformation (strain) and independent of the speed at which this takes place. Some solid materials do not obey Hooke's law, so they present non-linear dependence between stress and strain.

Viscous behavior is a characteristic of fluids. When an external force is applied to them, they deform (flow). The deformation continues as long as the force is maintained and ceases (without restoration) when it is removed. In the simplest cases, the rheological properties of fluids can be described by Newton's law, according to which the force applied is directly proportional to the speed of deformation but is independent of the latter. There are viscous fluids that do not obey Newton's law and, therefore, show non-linear dependence between the force and the speed of deformation. They are known as "non-Newtonian fluids".

Between elastic behavior and viscous behavior, many intermediate behavior patterns are found. For food technology, the most important case is that of complex materials, which present a rheological behavior that classes them as belonging to an intermediate zone between liquids and solids. These materials are called "viscoelastic" substances.

## 10.2.1 Viscous Behavior

### 10.2.1.1 Newtonian Fluids

There is an intuitive awareness that the viscosity of a fluid represents its difficulty in flowing. Consider a fluid contained between two large, flat, parallel plates (Figure 10.1). The system is initially at rest but, at a certain moment, the upper plate starts moving in direction x, at a constant velocity v, under the influence of force F. Force F must be applied to move the upper plate because the fluid exerts a drag that opposes its motion.

The quotient of force F and the area of the plate S is called the deformation force or shear stress ($\sigma = F/S$). The effect of the shear stress is a continuous deformation of the fluid which leads to some parts of it moving in relation to others (flow). After sufficient time has passed, a gradient of velocities is established like that shown in Figure 10.1 for the stationary system. Note that while shear stress in solids causes a certain relative deformation that is constant over time (strain, $\gamma$), in fluids the deformation increases continuously as time passes. The relevant quantity is no longer $\gamma$ but its variation over time, i.e., the gradient of speeds or shear rate ($\dot{\gamma} = dv/dy$).

For Newtonian fluids, the relationship between shear stress and shear rate is:

$$\sigma = \mu \cdot \dot{\gamma} \tag{10.1}$$

where $\mu$ is the Newtonian viscosity, a constant that is characteristic of the nature and physical conditions of the fluid. This equation is known as Newton's law of viscosity and the fluids that obey it are called Newtonian fluids. In the international system, the unit of viscosity is the Pa·s. The CGS unit is the poise (p), which differs from the Pa·s by a factor of 10 (10 p = 1 Pa·s).

### 10.2.1.2 Non-Newtonian Fluids

Fluids that do not obey Newton's law of viscosity are called non-Newtonian fluids. In practice, non-Newtonian fluids are encountered more frequently than Newtonian fluids.

A Newtonian fluid has the same viscosity irrespective of the shear rate. In non-Newtonian fluids, on the other hand, there is no linear relationship between shear stress and shear rate, so for each pair of $\sigma$ and $\dot{\gamma}$ values, there is a viscosity value $\sigma/\dot{\gamma}$, which is known as apparent viscosity, $\eta$.

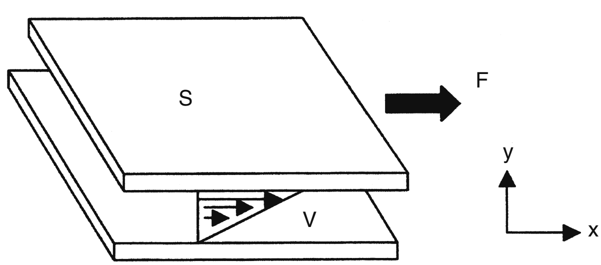



**FIGURE 10.1** Laminar flow of a fluid contained between two parallel plates.

The most elementary classification of non-Newtonian fluids refers to the presence or absence of a yield stress (Ferguson and Kembloski 1991), defined as the shear stress at which the material begins to flow (below the threshold value, the material behaves as an elastic solid).

Fluids without yield stress do not need a shear stress threshold value to start flowing; they are classified as pseudoplastic fluids and dilatant fluids. Their characteristic rheograms are shown in Figure 10.2 as curves (b) and (c), respectively. For comparison, this figure also shows the characteristic rheogram of a Newtonian fluid (a), which also lacks a flow threshold.

Because the viscosity corresponds to the slope, it can be seen that in the pseudoplastic fluids (curve b), the viscosity is greater for small $\sigma$ values than for high $\sigma$ values. In other words, the apparent viscosity decreases as the shear rate increases. In dilatant fluids (curve c), the opposite trend occurs: an increase in shear stress gives rise to a proportionally lower increase in the shear rate. In other words, the apparent viscosity increases as the shear rate increases (Barnes, Hutton, and Walters 1989).

Fluids that possess yield stress are characterized by requiring a shear stress value, $\sigma_0$, to start flowing; they are usually known as viscoplastic fluids. The rheogram in Figure 10.3 shows the characteristic curves of this type of fluid. It will be seen that the response may be linear as in (a) behavior analogous to that of a Newtonian fluid (linear viscoplastic fluid or Bingham plastic fluid) or non-linear as in (b) and (c) non-linear behavior (non-linear viscoplastic fluid or non-Bingham plastic fluid).

## 10.2.2 Viscoelastic Behavior

Viscoelastic substances are those that present a rheological behavior that classes them as belonging to an intermediate zone between liquids and solids.

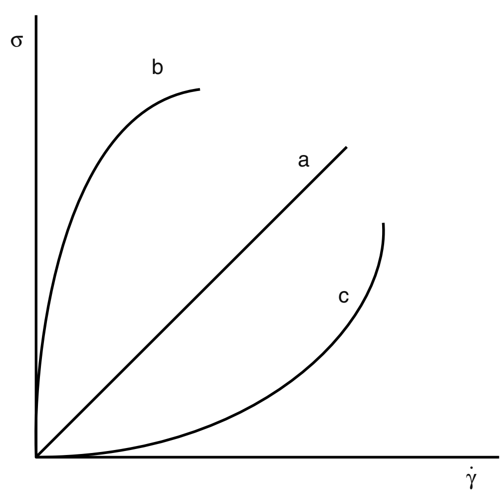



**FIGURE 10.2** Rheograms for fluids without yield stress: (a) Newtonian fluid, (b) pseudoplastic fluid, (c) dilatant fluid.

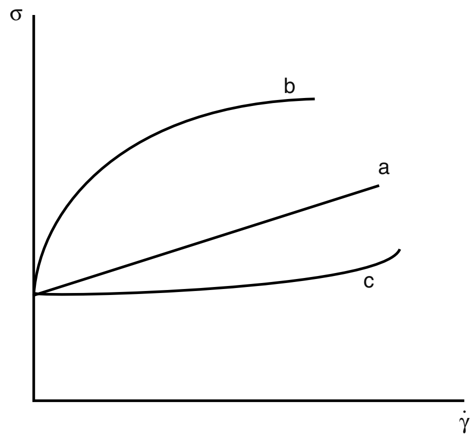



**FIGURE 10.3** Rheograms of plastic fluids: (a) Bingham plastic fluid, (b) and (c) non-Bingham plastic fluids.

To varying extents they are elastic and viscous, and are therefore termed viscoelastic (Schramm 1994).

When the relationship between stress and deformation in relation to time can be described by linear differential equations with constant coefficients, the behavior is termed linear viscoelastic. A relationship of this type implies that in an experiment, the force/deformation ratio will depend on time and not on the force or the deformation (Barnes, Hutton, and Walters 1989; Darby 1976). In a linear viscoelastic test, the sample does not suffer irreversible structural destruction. These tests, which provide important information on the original structure of the food, can be static or dynamic (Shoemaker et al. 1992).

Dynamic tests are an increasingly common way to study the viscoelastic behavior of foods. These tests are carried out by applying a force or deformation that continually varies in a sinusoidal manner over time and recording the response of the material to this variation. They are useful in many applications, for instance, for measuring the strength of a gel, starch gelatinization, protein coagulation or denaturation, texture development in bakery products or curd formation in cheeses (Steffe 1992).

In this type of analysis, the two controlled variables are frequency ($\omega$) and the maximum amplitude of the deformation applied ($\gamma_0$). The response of the material is measured by the maximum amplitude of the force developed ($\tau_0$) and the phase difference between the two waves ($\delta$). It can also be carried out in reverse, i.e., by applying a sinusoidal stress and recording the deformation it causes.

In these tests, the material under study is subjected to a periodic sinusoidal deformation which can be expressed with respect to time:

$$\gamma = \gamma^0 \sin \omega t \tag{10.2}$$

where $\gamma$ is the shear deformation, $\gamma^0$ is the maximum shear deformation or wave amplitude of the simple harmonic motion, $\omega$ is the frequency, and t is the test application time.

The speed of shear deformation or shear strain rate is also a periodic function:

$$\dot{\gamma} = d\gamma/dt = \gamma^0 \omega \cos \omega t = \dot{\gamma}^0 \cos \omega t \quad (10.3)$$

When a material is subjected to a small sinusoidal deformation, guaranteeing a linear viscoelastic response, after a certain number of cycles it will respond with a shear stress that also follows a sinusoidal function with time, at the same frequency but with an amplitude characteristic of the material nature. If the material behaves as an ideal solid, the response will be purely elastic, so the shear stress will be linearly dependent on the deformation ($\sigma = G\ \gamma$). Consequently the shear strain and shear stress will be in phase (Figure 10.4a):

$$\sigma = G \gamma \sin \omega t \quad (10.4)$$

If the material is an ideal viscous fluid, it will obey Newton's Law ($\sigma = \eta(d\gamma/dt)$) and the shear stress wave will be 90° out of phase with the shear strain wave (Figure 10.4b).

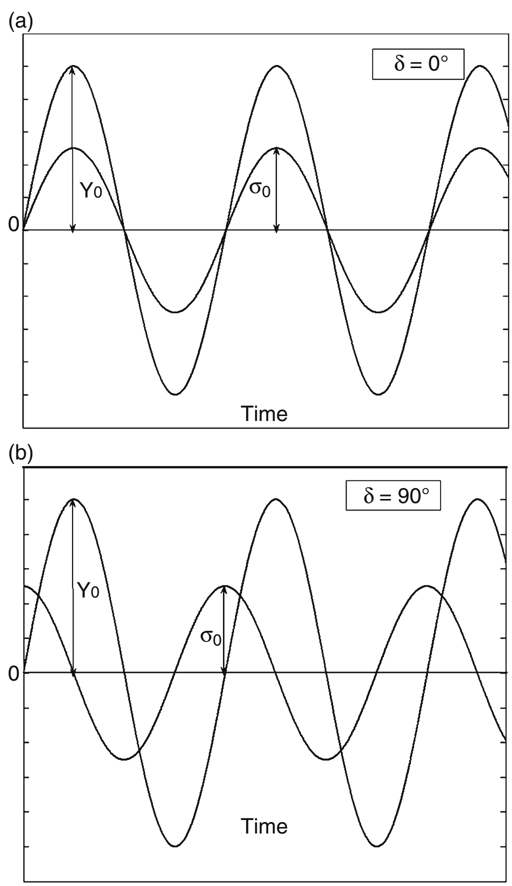



**FIGURE 10.4** Stress and strain waves for an ideal solid (a) and an ideal liquid (b).

$$\sigma = \eta\dot{\gamma}^0 \cos\omega t = \sigma^0 \cos\omega t = \sigma^0 \sin(\omega t + 90) \tag{10.5}$$

The behavior of a viscoelastic material lies between the pure viscous and pure elastic patterns, so the phase difference angle between the shear stress wave and the shear strain wave will be between 0° and 90°. The shear stress can be expressed mathematically as:

$$\sigma = \sigma^0 \sin(\omega t + \delta) \tag{10.6}$$

where $\sigma^0$ is the amplitude of the shear stress wave (maximum stress value) and $\delta$ the phase angle difference in relation to the strain, also referred to as the mechanical loss angle (Dealy 1982).

A further parameter used to study the dynamic test results is the complex modulus, G*. It is defined as the quotient of the force amplitude and the deformation amplitude ($G^* = \sigma_0/\gamma_0$) and represents the total resistance of a material to the deformation applied (Schramm 1994). It should be pointed out that in viscoelastic materials, the G* modulus also depends on the wave frequency. It can be broken down into two parts, one real and the other imaginary, as complex number notation is used to define it:

$$G^* = G' + iG'' = |G|\cos\delta + i|G|\sin\delta \tag{10.7}$$

$$|G| = \sqrt{(G')^2 + (G'')^2}$$
$$\text{where } G' = G^*\cos\delta = \frac{\tau_0}{\gamma_0}\cos\delta \quad \text{and} \quad G'' = G^*\sin\delta = \frac{\tau_0}{\gamma_0}\sin\delta \tag{10.8}$$

G' is called the storage or elastic modulus and represents the energy that the system stores temporarily and can later recover. G'' is called the viscous or loss modulus and represents the energy that the system uses at the start of flow, which is irretrievably lost in the form of heat.

In the case of a purely elastic material, the response to a dynamic deformation does not exhibit any phase difference, in other words $\delta = 0$, so the relationship between the force and the maximum amplitude is $\sigma_0 = G'\gamma_0$. A purely viscous fluid, on the other hand, presents a 90° phase difference, so the relationship between force and deformation is $\sigma_0 = G''\gamma_0$.

In viscoelastic materials, which possess elastic and viscous properties, the $\delta$ value is between 0° and 90° and the general expression of force in relation to deformation is:

$$\sigma = G'\gamma_0 \sin(\omega t) + G''\gamma_0 \cos(\omega t) \tag{10.9}$$

where $\gamma_0$ represents the maximum dynamic deformation amplitude.

The ratio of the G' and G'' moduli gives rise to another very important parameter which provides a direct index of the phase difference between force and deformation:

$\tan\delta = G''/G'$. Tan δ, which shows the relationship between the loss modulus and the storage modulus, provides a measurement of the relative proportion of viscous and elastic properties in a viscoelastic material. If G" is much greater than G", the material will behave in a similar fashion to a solid, and the strains applied will be elastic and recoverable. If G" is far larger than G', the energy employed in deforming the material will dissipate and will not be recovered.

Dynamic rheological methods are directly related to the molecular interactions and structure of the system to be studied. Depending on the frequency-dependence of the elastic modulus (G') and loss modulus (G"), three types of system can be described: macromolecular solutions ($G'' < G'$, where both parameters are highly frequency-dependent), weak gels ($G' < 10G''$, where both are frequency-dependent) and strong gels ($G' > 10\ G''$, where G' is independent of the frequency).

## 10.3 THE IMPORTANCE OF RHEOLOGY IN BATTERED FOOD MANUFACTURING

The importance of rheology in many food manufacturing industries is well recognized. The science of rheology has applications in food acceptability, food processing and food handling (Barbosa-Cánovas et al. 1996). Knowledge of the rheological and mechanical properties of various food systems is relevant in the design of flow processes, for quality control, in predicting storage and stability measurements, and in understanding and designing texture.

In the specific situation of battered food manufacturing, the rheological properties of the raw batter have a decisive role in the final quality of the battered food. They determine, directly or indirectly, most of the quality attributes of the final battered food. Raw batter rheology may determine the success of a battered food more than any other characteristic. The quantity and quality of batter pick-up, the adhesion, the appearance, the texture and the moisture and oil contents of the products are properties that can be related to raw batter rheology (Mukprasirt, Herald, and Flores 2000).

Due to this important role, raw batter viscosity is routinely monitored during the industrial production process. Monitoring takes place after the mixing step. The mixing step is the first step in the manufacturing process. It consists of mixing the dried batter ingredients homogeneously with water. The objective of the mixing step is to achieve good humectation of all the batter particles so that their optimum functionality is achieved. Viscosity development within the batter is mainly related to water-binding capacities and to the solubility of the dry ingredients. It is very important to spend the appropriate time on it for correct mixing. Undermixing a batter has more detrimental effects on fried food quality than overmixing a batter (Lee, Ng, and Steffe 2002; Suderman 1983). Many batter ingredients are insoluble at ambient or refrigerated temperatures, so an appropriate viscosity is necessary to keep them in suspension and to prevent undesirable stratification. If an adjustment in batter viscosity is necessary, it must be carried out before the batter enters the batter applicator. The commonest way to adjust viscosity is by varying the water-to-solids ratio. Incorporation of native starch or corn flour has been found to be a convenient way to increase the solid content without a significant effect on batter viscosity. The dry

miller can vary corn flour viscosity from thin to thick while maintaining the same ratio of solids to water in the test slurries (Burge 1990). Temperature control may be necessary in some special situations. For example, the viscosity development and water retention properties of batters containing methyl cellulose (MC) are enhanced at low temperature due to more effective hydration of the hydrocolloid (Sanz, Salvador, and Fiszman 2004a).

When applying the batter to the substrate (Figure 10.5), the amount of batter that adheres to the food passing through the applicator largely depends on its viscosity. Another factor is the conveyor belt speed. The batter viscosity is sometimes adjusted to suit the conveyor belt speed. In most cases, there is a linear relationship between the viscosity of the batter and coating pick-up, i.e., the quantity of batter that adheres to the substrate food. In principle, the greater the viscosity of the batter, the greater is the percentage that the substrate retains. For example, this occurs when part of the wheat flour is replaced by soy flour or rice flour (which respectively increase

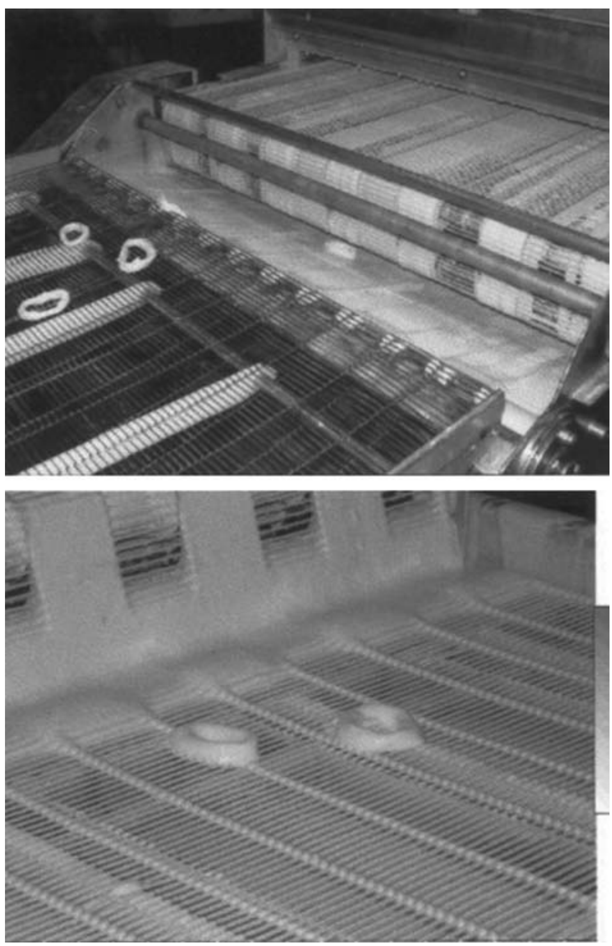


**FIGURE 10.5** Battering step during battered food manufacturing.

or decrease the viscosity and coating pick-up) (Dogan, Sahin, and Sumnu 2005a), by soy protein isolate (increased viscosity and coating pick-up), or by whey protein isolate or egg albumen (decreased viscosity and coating pick-up) (Dogan, Sahin, and Sumnu 2005b). The same linear relationship was found by Sanz, Salvador, and Fiszman (2008a) in batters to which they had added different types of resistant starch. Including pre-gelatinized starch in a batter formula increased the coating pick-up in comparison with the control and to other starch types due to its higher water-binding capacity (Altunakar, Sahin, and Sumnu 2004; Lee and Inglett 2006). Nonetheless, direct correlation between viscosity and coating pick-up did not hold true in some studies. The increase in viscosity caused by a higher concentration of HPMC, for instance, did not cause a proportionate increase in the quantity of batter on the final product. Consequently, viscosity is not the only factor determining coating pick-up (Meyers 1990). In addition, there is an appropriate viscosity range; too viscous a batter may produce uneven and lumpy crusts (Lee and Inglett 2006).

Batter adhesion has also been positively correlated with apparent viscosity in flour-based batters (Hsia, Smith, and Steffe 1992). In breading chicken drumsticks, an increase in batter viscosity caused by reducing the amount of water in the batter increased the breading picked up, improved adhesion and decreased cooking losses (Cunningham and Tiede 1981).

Other steps in the battered food manufacturing process where viscosity has a functional role are pre-frying and final frying. The viscosity of the batter influences the performance of the gas bubbles released by the leavening agent and of the steam produced due to water evaporation, which have a definitive impact on the final volume, texture, porosity and oil absorption during frying of the battered food product. Increased porosity has been positively correlated with oil uptake during the frying process (Pinthus, Weinberg, and Saguy 1995).

In some cases, an increase in viscosity resulting from an increase in the water retention properties of the batter has been associated with a decrease in oil absorption during frying. This is the usual situation when hydrocolloids are included in a batter formula. Along with other functional properties, the high water-retention properties of many hydrocolloids, especially those derived from cellulose such as MC and HPMC, contribute to their ability to increase viscosity and reduce oil absorption (Meyers 1990). It is generally recognized that oil uptake is related to moisture loss during frying (Lamberg, Hallstorm, and Olsson 1990; Saguy and Pinthus 1995).

In the case of MC and HPMC, their oil and moisture barrier properties are also attributed to their thermal gelation ability. Dynamic tests in the linear region have been found to be very useful for studying the thermo-rheological properties of a substance. Small amplitude oscillatory shear allows the changes induced by temperature to be monitored without altering the evolving sample structure. Figure 10.6 shows the effect of MC incorporation on the thermal properties of a batter upon applying an up and down temperature sweep. Figure 10.6 shows how the addition of MC influences the thermal behavior of the batter. In the MC batter, the initial increase in temperature provoked a clear decrease in G' until a minimum value was reached at a temperature of about 28°C. Above this critical temperature, the gelation process was triggered, as demonstrated by the dramatic increase in the modulus. At the beginning of the downward temperature ramp, the decrease in G' can be attributed

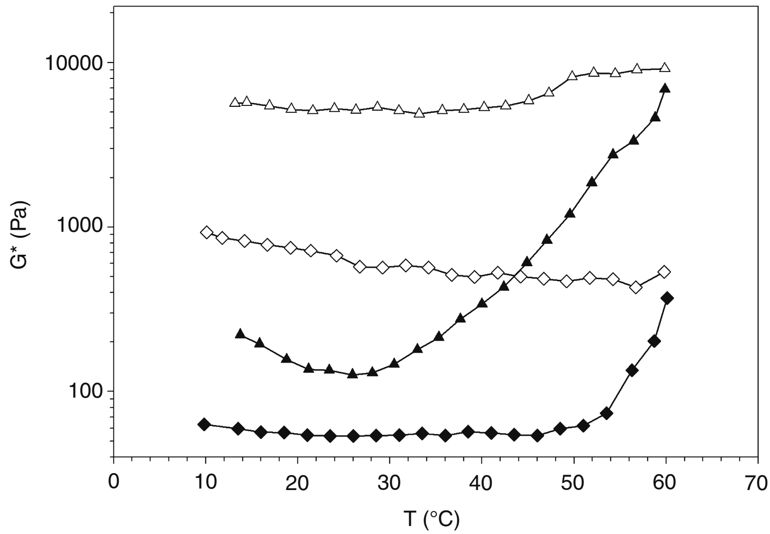



**FIGURE 10.6** Effect of MC incorporation on the thermal properties of a batter. Diamonds: conventional batter, triangles: batter with 1.5% MC. Heating curve: closed symbols, cooling curve: opened symbols.

to MC, which promotes thermo-reversible behavior. In the batter without MC, G' only began to rise when a typical starch gelatinization temperature was reached, and no decrease in G' was found during the cooling ramp; conversely, a steady increase in its values was observed (Sanz et al. 2005b).

Apart from hydrocolloids, the incorporation of steam jet-cooked barley flour in a batter increased the water-holding capacity which, apart from increasing the batter viscosity, was also associated with a decrease in oil absorption (Lee and Inglett 2006). Adding soy flour to a batter also increased viscosity and reduced oil absorption (Dogan, Sahin, and Sumnu 2005a). However, rice flour decreased viscosity and also reduced oil absorption; in this case the effect was associated with lower levels of hydrophobic wheat gluten in the batter formula. Due to its leavening effect, wheat gluten also increases porosity, enhancing moisture release (Dogan, Sahin, and Sumnu 2005a; Shih and Daigle 1999). If the batter ingredients have poor film-forming or water-retention properties, the increase in viscosity does not provide an effective oil-resisting barrier for the battered food (Shih and Daigle 1999).

## 10.4 INFLUENCE OF BATTER INGREDIENTS ON RHEOLOGICAL PROPERTIES

### 10.4.1 Wheat Flour

Wheat flour is typically the major constituent of batter formulations and determines their fundamental characteristics. The functionality of wheat flour in battered food focuses upon the complementary actions of its major components: starch and protein (Loewe 1990; 1993).

#### 10.4.1.1 Wheat Protein

The increase in batter viscosity during batter mixing is mainly due to gluten development. Depending on the quantity and, to some extent, the quality of the gluten and the available water, the resultant structure can be as firm as bread dough or as flowing as batter. Hard wheat flours, due to their higher protein content, require more water than soft wheat flours to yield comparable viscosities when used in a batter. This results from the efficient water-binding capacity of the gluten protein (Davis 1983). In puff/tempura batters, gluten protein retains the gas formed due to the leavening effect. The result is an aerated, porous batter, which is essential for a proper texture and crispness.

#### 10.4.1.2 Wheat Starch

Wheat starch is composed of linear and branched polymers of glucose (amylose and amylopectin, respectively). The ratio of these polymers has a profound effect on wheat flour functionality.

In the intact cereal grain, the starch granules are embedded in a protein matrix. The degree of binding between the protein and starch and the milling process used to separate them affect the degree of starch damage and the particle size distribution of the resulting flour. Starch damage and flour particle size affect the functional properties of flours.

Flour from hard wheat tends to contain a greater proportion of damaged starch than flour from soft wheat. This is because the starch and protein tend to be more tightly bonded in hard wheat grains; therefore the milling process causes some disruption of the starch granule structure. Damaged starch granules have a higher water-absorption capacity than undamaged starch granules, so if flours with a large amount of damaged starch are used, more water is needed to obtain a standard viscosity.

When heated in the presence of water, starch undergoes gelatinization. In the original granule structure, a considerable portion of starch exists in crystalline form which, at moderate temperatures, is impervious to water. Upon heating, these areas are broken down and are exposed to water, resulting in swelling of the granule. Additionally, amylose is released and contributes to the increase in viscosity.

When there is an excess of water, wheat starch gelatinization takes place at between 52°C and 63°C. In systems such as batters, where the quantity of water is limited and different ingredients may be competing for it, starch gelatinization may take place at higher temperatures. If the available water is very limited, gelatinization may not be completed and, in extreme cases, it may not occur. Figure 10.7 shows the influence of salt and corn flour on the gelatinization temperature of wheat flour by monitoring the evolution of the storage modulus (G') on increasing the temperature. The point where G' increases with temperature, reflecting an increase in the consistency of the system, is considered to be an indication of the beginning of the gelatinization process. The addition of salt or corn flour (6%) delayed the temperature at which G' started to increase: both delayed the beginning of wheat starch gelatinization, although the effect was clearly more evident in the case of salt.

A batter should be sufficiently viscous to guarantee the homogeneous distribution of starch and simultaneously contain enough water to assure proper starch

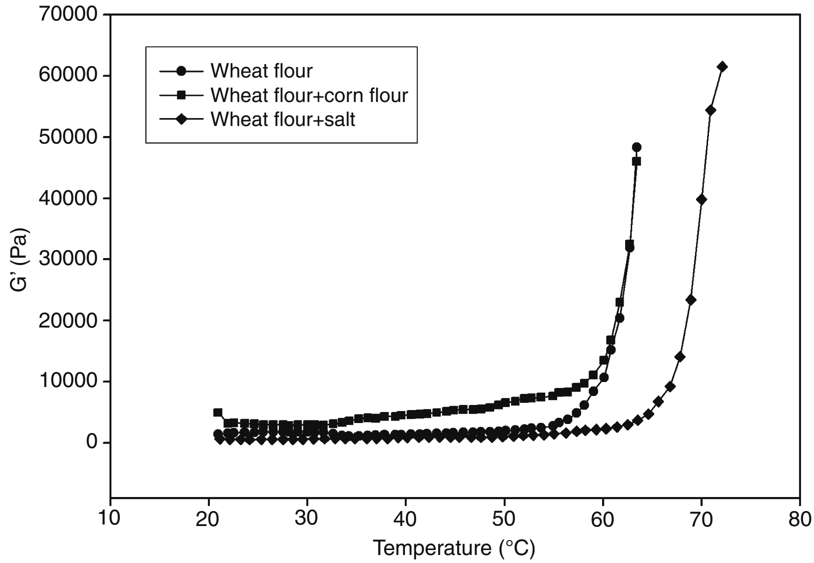



**FIGURE 10.7** Influence of salt and corn flour on the viscoelastic properties of wheat flour upon heating.

gelatinization. Starch gelatinization together with wheat protein constitutes the final structure of the battered product.

## 10.4.2 Other Flours

### 10.4.2.1 Corn Flour

A long-established use of corn flour in batter systems is as a viscosity controller. Through the blending of corn milling fractions, the miller can supply corn flours to make flour/water slurries with a wide range of viscosities but equivalent solid contents (Burge 1990).

Corn flour (3–6% dry mix) can be used to increase the total solid content of a batter without significantly altering batter viscosity (Salvador, Sanz, and Fiszman 2003).

### 10.4.2.2 Rice Flour

Rice flour provides an alternative to wheat flour in batter formulations. The high proportion of starch in rice flour makes it absorb less oil than wheat flour does during frying. Also, because it does not contain gluten, batters prepared with rice flour are suitable for those with celiac disease.

The absence of gluten results in very low viscosity. Therefore, to achieve good final product quality, the rice flour must be combined with thickeners. The incorporation of pre-gelatinized rice flour and phosphorylated rice starch has given good results in chicken nugget batters; their use also contributes to the oil-reduction properties of the rice flour, given their ability to form a film (Shih and Daigle 1999; Shih

and Daigle 2001). Rice flours made from long-grain rice gave rise to less oil absorption during frying than those made from waxy rice (Shih and Daigle 1999). This lower absorption is associated with their higher amylose content.

As well as maize and rice flours, soy and barley flours have also been used in batters, mainly to increase their adhesion and water-retention capacity (Loewe 1990).

### 10.4.3 Starches

Starches have an important role in batters and perform various functions. Native starches are used in combination with flour in batter formulations. They provide a functional effect comparable with reducing the protein and/or damaged starch levels of the flour (Davis 1983). Changes in the starch to wheat flour ratio are very useful for adjusting the variations in the flour.

Various modified starches are also available. Modifications have a key role in the functionality of the starch, as well as in the batter. Starches are modified to improve functional properties and impart others not found in native starch. Modifications that are relevant to batter systems are oxidation, substitution, dextrinization and pre-gelatinization (Beirendonck 2001; Shinsato, Hippleheuser, and Van Beirendonck 1999).

Modifying starch by oxidation consists of an initial depolymerization of the polysaccharides followed by the oxidation of small number of hydroxyl and aldehyde groups to carboxyl groups. The carboxyl groups of the oxidized starch bind to the proteins of the substrate, increasing adhesion. These starches can be used at high concentrations without causing a significant increase in viscosity.

Starch modification by substitution consists in introducing substituents into the hydroxyl groups. The substitution takes place in an aqueous suspension of granulated starch in the presence of acetic anhydride or propylene oxide. The substituents introduced do not encourage the association of polysaccharide chains by hydrogen bonds, so retrogradation is delayed or avoided altogether. Substitution also causes a reduction in the gelatinization temperature of the starch because the acetate groups joined to the starch polymer make its structure more open, assisting its permeability to water. During frying, starch substitution allows the release of amylose which, when it retrogrades, gives rise to the formation of a film around the substrate. This film acts as a barrier to the loss of moisture and the entry of oil.

Acid hydrolysis of starch through a dry reaction at high temperatures followed by repolymerization produces dextrins with different solubilities and viscosities, and with excellent adhesion, clarity and bonding properties. The viscosity contributed by the dextrins is very small, owing to their low molecular weight. White dextrin can be used at percentages of up to 55% of the total solids. Viscosity and solubility depend on reaction conditions. As conversion increases, so does the cold water solubility of the dextrins. The use of dextrins in batters reduces the viscosity of the batter and results in batter-coated squid rings that retain their crispness for longer after frying (Baixauli et al. 2003; Sanz et al. 2005a; Shinsato, Hippleheuser, and Van Beirendonck 1999). Figure 10.8 shows the effect of incorporation of dextrin and dried egg on the flow properties of a standard batter. Throughout the shear rate range studied, the incorporation of dextrin decreased the apparent viscosity values, while the incorporation of dried egg produced the opposite effect. Unlike protein ingredients, polysaccharides cause a decrease in the viscosity or consistency of the batters,

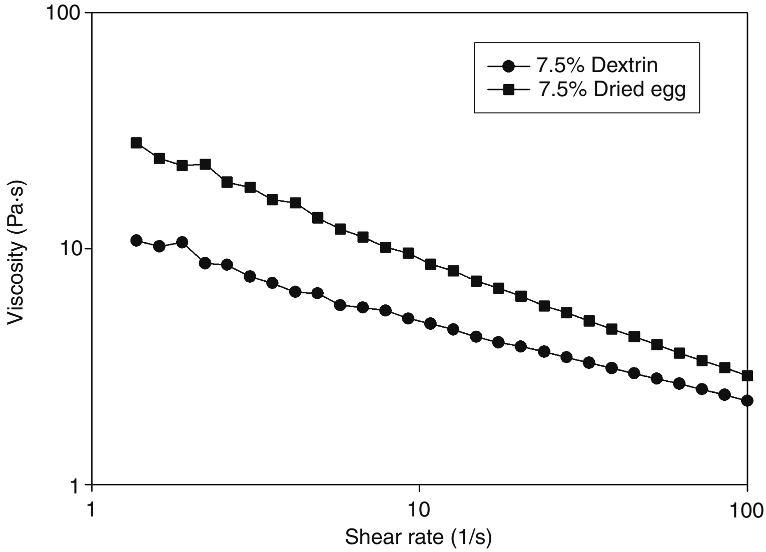



**FIGURE 10.8** Influence of dextrin and dried egg in the flow properties of a batter.

mainly because they dilute the wheat flour proteins which are the main thickening agents at low temperatures. This effect is also reflected in a lowering of the viscoelastic constants G' and G" (Sanz et al. 2005a).

Pre-gelatinized starch is obtained by heating the starch in water until it gelates, then subjecting it to a drying process. Pre-gelatinized starches are used at low concentrations to increase viscosity and keep solids in suspension. They present viscous synergy in combination with some gums.

Resistant starches (RS) are another type of starch that has recently been tested in batter systems. Resistant starch is defined as the sum of starch and products of starch degradation not absorbed in the small intestine of healthy individuals (Asp and Björck 1992). The interest in RS comes from its positive health benefits. Some of the benefits are like those of traditional fiber and others are unique to RS. There are different types of RS and they affect batter viscosity differently. Replacement of 15% wheat flour by granular RS (RS2 type) produced from high-amylose maize has been found to significantly reduce batter viscosity, whereas replacement with an RS3 type obtained from high amylose maize starch increased batter viscosity (Sanz, Salvador, and Fiszman 2008a). At the 15% replacement level, none of the RS types affected the heating profile of the batter measured by small-amplitude oscillatory shear over 20–85°C. Incorporation of retrograded starch from high amylose maize into a batter formula containing MC did not affect the pattern of behavior upon heating the batter (Sanz, Salvador, and Fiszman 2008b).

### 10.4.4 Proteins

In general, the addition of proteins increases the consistency of raw batter by strengthening its protein structure. This is reflected by a rise in the viscosity and the viscoelastic constants G' and G" of the batter (Baixauli et al. 2003; Sanz et al.

2005a). The effect of gluten and dried egg incorporation (7.5%) on the mechanical spectra of a batter is shown in Figure 10.9. Both ingredients increase the viscoelastic functions, although the effect has been found to be more evident for gluten. Also, gluten was more effective than dried egg for increasing the viscosity of the raw batter (Sanz et al. 2005a).

Incorporation of soy protein isolate into a batter formula increased apparent viscosity, while incorporation of whey protein isolate and egg albumen decreased it (Dogan, Sahin, and Sumnu 2005b).

### 10.4.5 Hydrocolloids

Hydrocolloids are defined as water-soluble polymers that can confer viscosity or gelate aqueous systems. One of the main applications of hydrocolloids in battered products is to precisely increase the viscosity of the batter. Examples are batters made with low-viscosity ingredients such as rice flour (Mukprasirt, Herald, and Flores 2000) or batters with low content of total solids. In both cases, the addition of the hydrocolloid not only increases the viscosity of the batter, but also helps to keep the solids in suspension, avoiding their precipitation and consequent unevenness in the food coating. The hydrocolloids used for this purpose can be hydrated in cold water, so they are easily added to the formulation simply by dry blending with other ingredients. Guar gum, xanthan gum and the cellulose derivatives CMC, MC and HPMC have been the most used (Hsia, Smith, and Steffe 1992; Sanz, Salvador, and Fiszman 2004a). Evidently, their viscosity-boosting efficiency varies, depending on the type of hydrocolloid and its concentration, so the choice depends on the specific needs of each product. The effect of the increase in MC concentration on the flow properties of a batter is shown in Figure 10.10. The flow curves reflect the shear

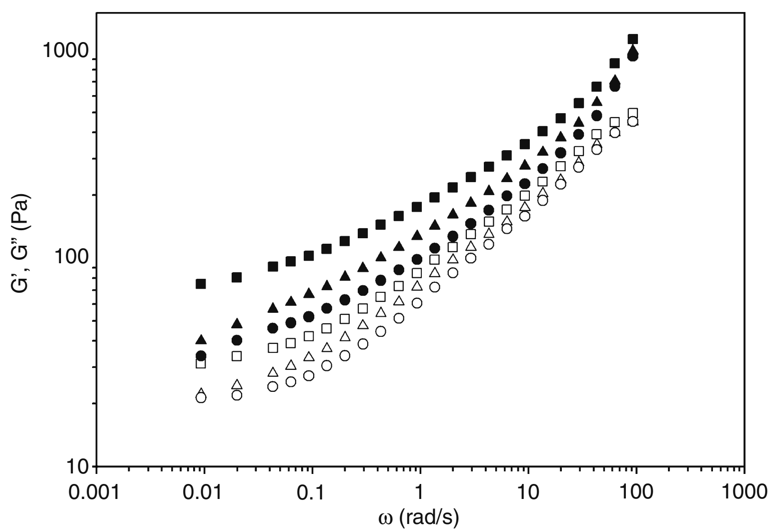



**FIGURE 10.9** Influence of gluten and dried egg in the mechanical spectra of a batter. Squares: batter with gluten, triangles: batter with dried egg, circles: conventional batter. G' values (solid symbols) and G'' (open symbols).

thinning behavior of the batter, which was well-fitted to the Ostwald de Waele model in the shear rate range studied. Increased MC concentration significantly increased the consistency index as well as the shear-thinning behavior (Sanz, Salvador, and Fiszman 2004a).

Compared with guar gum and CMC, xanthan gum imparted greater viscosity (Hsia, Smith, and Steffe 1992). In the case of xanthan gum and guar gum, increasing the concentration from 0.25% to 1% increased the consistency index of the batters and their pseudoplasticity, whereas increasing the concentration of CMC did not significantly increase the consistency index and gave rise to a reduction in pseudoplasticity. When MC is employed, cold water must be used to prepare the batter to ensure adequate hydration for its properties to develop. Equally, to maintain suitable functionality, it is advisable to refrigerate the batter during the battered food manufacturing processes (Sanz, Salvador, and Fiszman 2004a, 2004b; The Dow Chemical Company 1996). An illustration of the influence of the raw batter temperature of MC-containing batters on the flow and on the fat and moisture barrier properties is shown in Figure 10.11 and Figure 10.12. Consistency (k) and fat and moisture barrier properties decreased significantly as the temperature rose from 5°C to 25°C. These results are the consequence of a decrease in MC hydration on temperature increase. The lower the temperature of the raw batter, the more effective will be viscosity development and the fat and moisture barrier properties.

Another property that is attributed to the use of hydrocolloids and is fundamentally related to the increase in viscosity they confer is increased coating pick-up and better adhesion of the batter to the food it is coating. There is generally a positive correlation between batter viscosity and the quantity of batter adhering to the substrate. This has been found to be the case for xanthan gum, guar gum and CMC in batters for chicken nuggets (Hsia, Smith, and Steffe 1992). However, in the case of HPMC, the greater

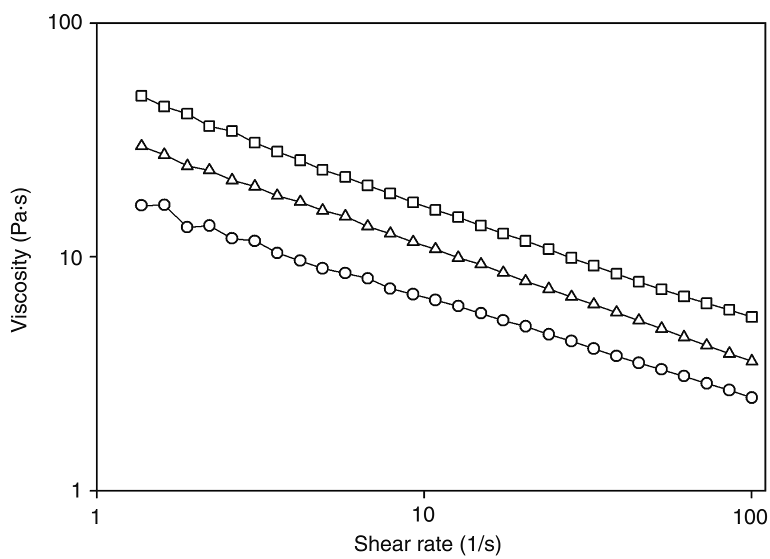



**FIGURE 10.10** Influence of MC concentration in the flow properties of a batter. Circles: 1% MC, triangles: 1.5% MC, squares: 2% MC.

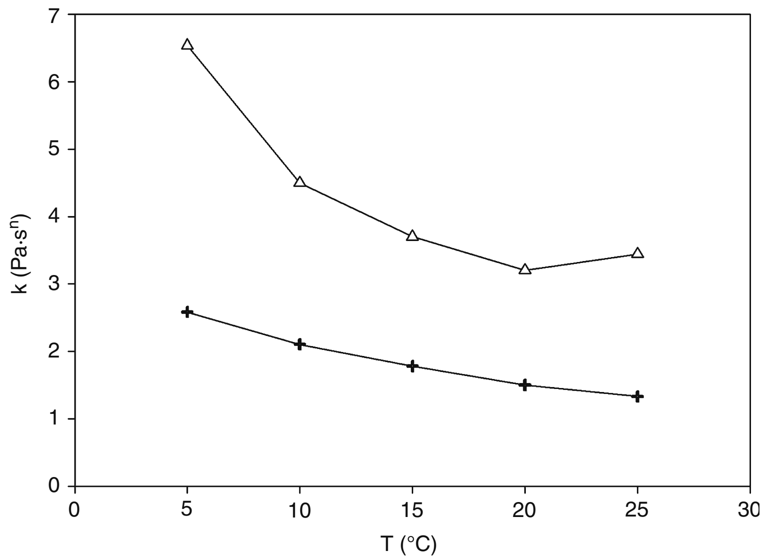



**FIGURE 10.11** Effect of raw batter temperature in the consistency index (k) for a standard batter (crosses) and for a batter with 1.5% MC (triangles).

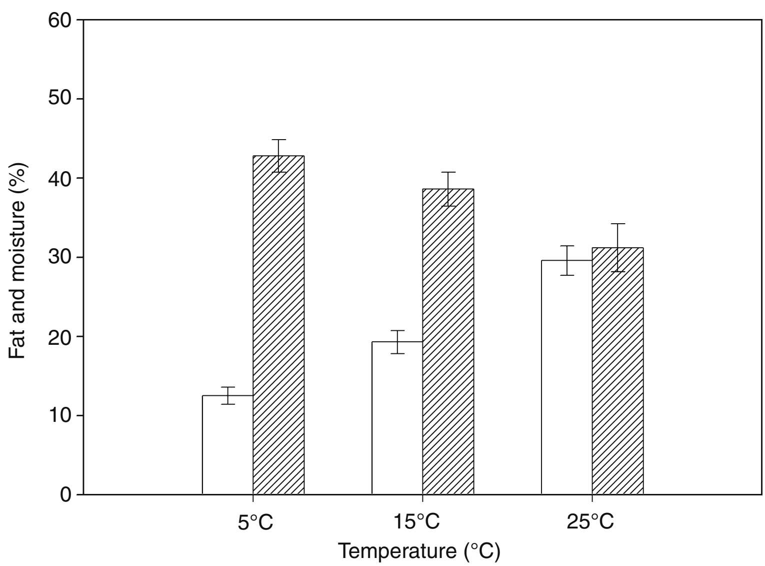



**FIGURE 10.12** Influence of raw batter temperature (5, 15 and 25ºC) of a MC batter in batter crust fat and moisture after final frying. White bars: fat content, shadow bars: moisture content.

batter viscosity brought about by increasing the hydrocolloid concentration did not greatly improve batter pick-up on chicken nuggets (Meyers 1990). In a study to determine the effect of different proteins and gums in improving batter adhesion to chicken

skin, gelatine and egg albumin were the proteins that gave the greatest adhesion; of the different gums studied (CMC, guar, tragacanth and xanthan), only CMC significantly increased adhesion and in no case did an increase in concentration have a significant effect on adhesion (Suderman, Wiker, and Cunningham 1981). The hot thermogelling capacity of MC and HPMC is also associated with improved adhesion because of the cohesiveness it imparts during frying; the gels formed by alginate, gellan gum and carrageenan have also been associated with better adhesion (Kuntz 1997). In rice flour-based batters, MC has also improved batter adhesion to chicken drumsticks immediately after frying, although its effectiveness was reduced after freezing, probably because the gum retained excessive moisture (Mukprasirt et al. 2001).

## 10.5 MEASUREMENTS OF THE RHEOLOGICAL PROPERTIES OF BATTERS

Due to its importance as a quality parameter, batter viscosity is routinely measured during the industrial manufacturing process. The instruments most commonly used to measure batter viscosity in industry are Zahn and Stein cups, the Bostwick consistometer, and the Brookfield viscometer (Burge 1990). To measure the rheological properties of a material, viscosimeters and rheometers must be used.

### 10.5.1 Zahn Cup and Stein Cup Viscosimeters

Zahn and Stein cups consist of a container with a hole at the bottom which is filled with the batter. The time required to empty the container is taken as an indicator of batter viscosity, or more precisely, of batter fluidity. The Zahn cup possesses a lower-diameter hole, making it the appropriate choice for measuring lower-viscosity batters. The higher-diameter hole of the Stein cup is more suitable for measuring higher-viscosity batters.

### 10.5.2 Bostwick Consistometer

The Bostwick consistometer is also very easy to use. The sample is placed in a compartment at one end of the instrument and allowed to flow along a slightly sloping surface. The flow distance is measured in relation to time. As with the Zahn and Stein cups, the Bostwick consistometer only provides an indication of the flow properties of the sample.

### 10.5.3 Brookfield Viscosimeter

In the Brookfield viscosimeter, the sample is placed in a wide container and the resistance of the sample to the rotation of a spindle is measured. The resistance values are translated into apparent viscosity values. One of its advantages is considerable versatility. There are different spindle sizes and measurements can be made at different rotational speeds, broadening the range of viscosities that can be measured. Due to the non-Newtonian behavior of batters, it is difficult to compare viscosity values measured in different laboratories. For the values to be comparable, the measurement conditions (spindle diameter, rotational speed, temperature) should be identical.

One important aspect is that these instruments provide only an indication of the rheological properties of the batter. The Brookfield viscosimeter even gives viscosity values, but given the non-Newtonian nature of the batters, they are apparent viscosity values. Its use under standardized conditions is very useful for comparisons, but it does not provide information on the real viscous behavior of the sample. Rheological properties should be independent of size, shape and how they are measured; i.e., they are universal. The viscosity of a batter measured in one laboratory will be identical to the one measured in any laboratory in the world, even if they are measured using different tests, samples sizes or shapes. Rheological measurements are fundamental tests and have the advantage, with respect to empirical tests, of determining true physical properties because they are based on known physical concepts and equations (Tabilo-Munizaga and Bárbosa-Cánovas 2005).

To characterize the rheological behavior of non-Newtonian fluids, as in the case of batters, it is also necessary to obtain a flow curve, which is the dependency between shear stress and shear rate over as wide as possible shear rate range. In addition, to characterize the viscoelastic properties of a material, an oscillatory shear needs to be applied to the sample.

### 10.5.4 Rotational Rheometers and Viscosimeters

Rotational viscosimeters and rheometers are those most commonly used to measure the rheological properties of batters. They employ rotation to achieve simple shear flow. They are classified into two types, depending on the way the flow is induced:

- Controlled shear rate, in which the rotating element turns at a particular speed and the resulting momentum is measured.
- Controlled shear stress, where a torque is applied and the resulting rotation speed is measured.

Depending on the type of measurement and the characteristics of the sample, different sensors with different geometries are used. The most frequently employed are described below.

#### 10.5.4.1 Coaxial Cylinder

In this geometry, the sample shears in the gap between two coaxial cylinders (Figure 10.13). Because the cylinders present a large surface in contact with the sample, this is the geometry of choice for measuring low-viscosity fluids.

The shear rate at the radius of the internal cylinder is proportional to the angular velocity ($\omega$) and the system geometry.

$$\dot{\gamma} = 2\omega \frac{R_a^2}{R_a^2 - R_i^2} \tag{10.10}$$

where $\dot{\gamma}$ is the shear rate at the radius of the internal cylinder in $s^{-1}$, $\omega$ is the angular velocity in rad/s, $R_a$ is the radius of the external cylinder in m, and $R_i$ is the radius of the internal cylinder in m.

The shear stress at the radius of the internal cylinder, in Pa, is:

$$\sigma_i = \frac{M_d}{2\pi L\, R_i^2\, Cl} \tag{10.11}$$

where $\sigma_i$ is the shear stress at the radius of the internal cylinder, $M_d$ is the torque to be determined in N·m, L is the height of the rotor in m and Cl is the correction factor for the rotor edge effects.

### 10.5.4.2 Cone-Plate

In this geometry, the fluid shears between a flat horizontal plate and a cone of radius R and a very small angle (Figure 10.14).

The shear rate is calculated by the following Equation:

$$\dot{\gamma} = \frac{\omega}{\tan\theta} \tag{10.12}$$

where $\omega$ is the angular velocity in rad/s and $\theta$ is the cone angle in rad, so $\dot{\gamma}$ is constant and uniform throughout the sample. If it is considered that for very small angle values $\tan\theta \approx \theta$, the Equation 10.12 will be:

$$\dot{\gamma} = \frac{\omega}{\theta} \tag{10.13}$$

The cone angle most commonly used is 0.0174 rad (1°). Cones with smaller angles are also available, but are less advisable because the adjustment of the distance

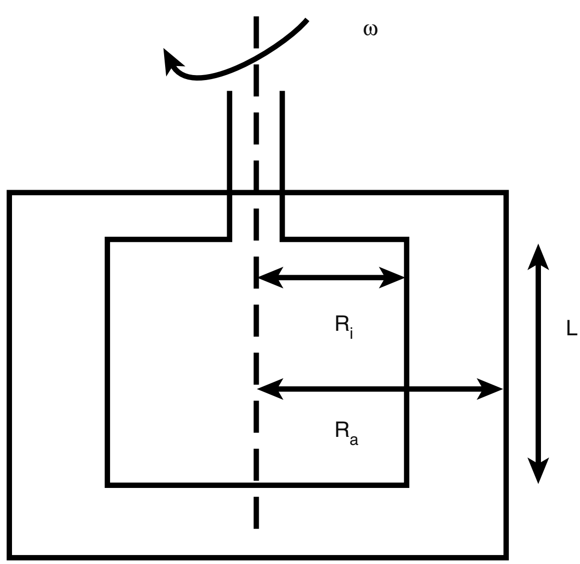



**FIGURE 10.13** Coaxial cylinder geometry.

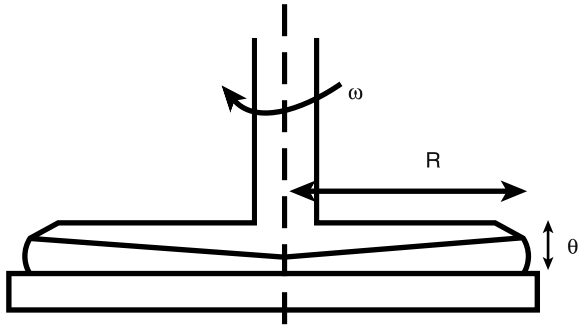



**FIGURE 10.14** Truncated cone and plate geometry.

between cone and plate becomes a highly critical factor. Cone angles of up to 4° are frequently used to measure dispersions.

The shear stress is proportional to the torque:

$$\sigma_c = \left(\frac{3}{2\pi R^3}\right) M_d \tag{10.14}$$

where $\sigma_c$ is the shear stress at the cone in Pa, R is the cone radius in m, and $M_d$ is the torque measured in N·m.

#### 10.5.4.3 Plate–Plate

In plate–plate geometry, the fluid is placed between two parallel horizontal discs of radius R and gap height h (Figure 10.15).

The gap height (h) can be varied, but should not be $< 0.3$ mm or $> 3$ mm. Plate–plate is the geometry of choice if the sample contains large-sized particles. The gap between the plates should be at least three times greater than the largest particle size in the sample.

In this geometry, the shear rate is as follows:

$$\dot{\gamma} = \frac{\omega R}{h} \tag{10.15}$$

where $\dot{\gamma}$ is the shear rate in $s^{-1}$, R is the plate radius in m, and h is the gap between the plates in m.

Consequently, in plate–plate geometry, the shear rate depends on the gap height of the plates and on their radius (from 0 at the centre to a maximum value at the external radius). It is usually measured at the external radius.

In the case of Newtonian fluids, the shear stress at the radius is proportional to the torque:

$$\sigma = M_d \frac{2}{\pi R^3} \tag{10.16}$$

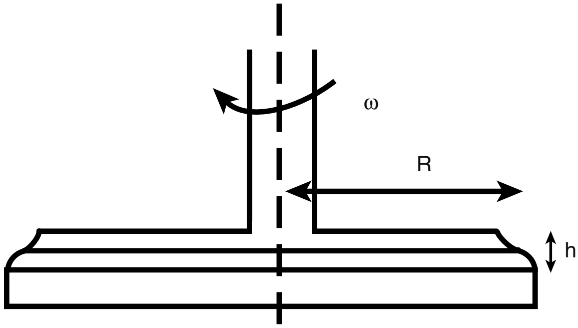



**FIGURE 10.15** Plate–plate geometry.

where σ is the shear stress in Pa, $M_d$ is the torque in N·m and R is the external radius of the plate in m.

In the case of non-Newtonian fluids that obey the power law, the shear stress is corrected by the following expression:

$$\sigma = M_d \frac{2}{\pi R^3}\left(\frac{3+n}{4}\right) \tag{10.17}$$

where n is the power index.

## 10.6 MODELLING THE NON-NEWTONIAN BEHAVIOR OF BATTERS

A system can respond to a particular shear stress in various ways. To describe these behavior patterns, several equations or mathematical models that relate shear stress to shear rate or viscosity to shear rate have been proposed.

### 10.6.1 Ostwald–De Waele Model

For fluids without yield stress, the simplest model is the Ostwald–de Waele model or power law:

$$\sigma = k \cdot \dot{\gamma}^n \tag{10.18}$$

where k and n are the rheological parameters of the model. The k parameter is known as the consistency index and n as the flow index. Because for $n = 1$ the expression reduces to Newton's law with $\mu = k$, the difference between n and 1 measures the deviation from Newtonian behavior. If $n < 1$, a rheogram that represents a pseudoplastic fluid is obtained. If $n > 1$, however, the characteristic rheogram is the one that represents a dilatant fluid.

Bearing in mind that apparent viscosity is defined by the quotient of shear stress and shear rate, the Ostwald–de Waele model can be expressed as:

$$\eta(\dot{\gamma}) = k\dot{\gamma}^{n-1} \tag{10.19}$$

The drawback of the Ostwald–de Waele model is, for example, that in the case of pseudoplastic fluids ($n < 1$), the model predicts that:

$$\eta(0) \to \infty$$

$$\eta(\infty) \to 0$$

so the equation is not valid for describing the way that viscosity behaves at very low or very high shear rates.

### 10.6.2 Herschel–Bulkley Model

To describe the behavior of fluids with yield stress, one of the most commonly used empirical models is the Herschel–Bulkley model:

$$\sigma = \sigma_0 + k\,\dot{\gamma}^n \tag{10.20}$$

where $\sigma_0$, k and n are the parameters of the model. For historical reasons, when $n = 1$, the above expression is known as the Bingham model:

$$\sigma = \sigma_0 + k\,\dot{\gamma} \tag{10.21}$$

where, k represents the viscosity of the system when flowing, known as the plastic viscosity.

### 10.6.3 Casson Model

Casson (1959) formulated a new model to describe the flow of non-linear viscoplastic fluids:

$$\sigma^{1/2} = \sigma_0^{1/2} + (k\dot{\gamma})^{1/2} \tag{10.22}$$

In this expression, $\sigma_0$ and k have the same meanings as in the Bingham model.

### 10.6.4 Cross Model

In general, predicting the general shape of the flow curves of non-Newtonian fluids requires separating the high and low shear regions, which demands four-parameter models. In these cases, the flow curves are characterized by three different regions (Figure 10.16):

1. Lower Newtonian region: low shear rates characterized by a constant limiting viscosity $\eta_0$.
2. Intermediate Newtonian region: intermediate shear rates characterized by a viscosity which is a function of the shear rate.
3. Upper Newtonian region: high shear rates characterized by a constant limiting viscosity $\eta_\infty$.

The Cross model is used to describe this type of fluids, based on the following Equation:

$$\frac{\eta-\eta_\infty}{\eta_0-\eta_\infty}=\frac{1}{1+\left(K\dot{\gamma}\right)^m} \tag{10.23}$$

where $K$ is a constant with dimensions of time and $m$ is a dimensionless parameter.

A simplification of the Cross model gave rise to the Sisko model (Sisko 1958), which is used to characterize Newtonian fluids at intermediate shear rates:

$$\eta=\eta_\infty+K\dot{\gamma}^{n-1} \tag{10.24}$$

where, for values of $\eta \ll \eta_0$ and $\eta \gg \eta_\infty$, the Ostwald–de Waele model is obtained.

The range of shear rates mainly studied in previous studies in batter systems corresponds to the intermediate region, therefore the Ostwald–de Waele model (Baixauli et al. 2003; Dogan, Sahin, and Sumnu 2005a, 2005b; Sanz, Salvador, and Fiszman 2004a; Salvador, Sanz, and Fiszman 2003) and the Herschel–Bulkley model (Asha, Susheelamma, and Guha 2007) have been successfully employed to characterize their shear thinning behavior.

## 10.7 CONCLUSIONS

In the past, the application of rheology in battered food was restricted to empirical measurements such as measuring apparent viscosity at a single rotational speed. These empirical methods are simple and very useful for quality control, but they cannot be used to improve batter properties or to gain a deep understanding of batter structure and behavior. The latest scientific research on the rheological properties of batters has outlined the usefulness and importance of fundamental rheological methods as tools for predicting and improving battered food quality. Fundamental rheological measurements allow structural changes due to batter ingredient composition or during batter processing to be monitored.

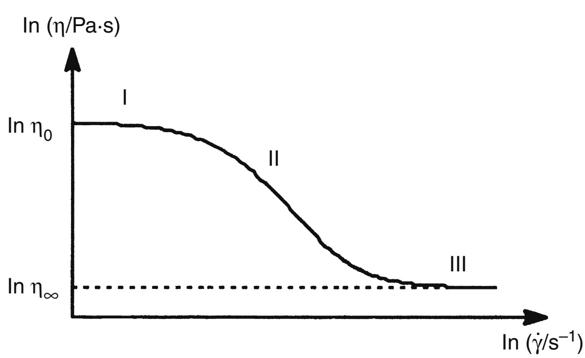



**FIGURE 10.16** General shape of the flow curve of a non-Newtonian fluid.

Future trends in battered foods are expected to continue towards the achievement of healthier products (mainly low fat) with crisper and more innovative textures. The development of convenient battered foods suitable for final cooking by methods other than frying is another future concern. The achievement of such objectives will entail the employment of new ingredients and/or processing conditions and, undoubtedly, the need to evaluate how they will affect the fundamental rheological properties of batters.

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# 11 Quality of Battered or Breaded Fried Products

*Susana Fiszman*

## CONTENTS



## 11.1 INTRODUCTION

Foods with a crisp/crunchy fried coating possess several characteristics that are much appreciated by consumers throughout the world. They are expected to possess certain properties of appearance, texture and flavor that add value to the product which is acting as a substrate (e.g., meat, chicken, vegetables, cheese). Coated fried foods have come a long way since the formulation of domestic kitchen batters based on egg and flour. Changing models of consumption and the rise in demand for convenience foods have resulted in high-value, innovative, and complex batter production technology. After a few minutes of frying, coated foods have a pleasant golden-colored exterior with a crisp/crunchy texture while the interior usually remains tender and juicy. These characteristics normally make these products very appetizing.

For a long time, chicken, fish, and onion rings were the best-known type of coated foods. However, the market has expanded enormously to include snacks

such as cheese sticks and vegetables such as mushrooms, cauliflower, zucchini, or broccoli.

The simplest batter can be just flour and water paste into which a product is dipped before it is fried. However, the list of ingredients is usually much longer (starch, gums, egg, other proteins, seasonings, and many other items) and batters have therefore become highly complex, sophisticated systems in which the functionality of the ingredients is very wide-ranging and their interaction determines the final performance of the product. In this type of coating, known as "tempura-type batter", when the liquid batter comes into direct contact with the hot frying oil, it sets around the piece of food and becomes a crisp crust. All the final quality characteristics of the tempura-type-coated food largely depend on good formulation of the ingredients that constitute the raw batter. The formulation has to achieve a system that provides a good coating, performs well during frying, and develops optimal texture, appearance, aroma and flavor properties. The nature of the ingredients selected for the formulation is fundamental in this type of coating: their viscosity and water-retention capacity, the characteristics of the proteins they contain, the temperature and proportion of water, or the addition of gums are just a few of the factors that must be borne in mind.

The other type of batter is adhesion batter, which acts as a "glue" for an external layer of breadcrumbs, creating a battered and breaded end product. The choice of the batter ingredients is not such a delicate matter as in tempura-type products. Essentially, the batter needs to act as a good adhesive. It coagulates during frying but cannot be distinguished by the consumer. The end-product characteristics mainly depend on the breadcrumb coating: the bread or grains from which it is made, shape and size of the particles, their regularity, and degree of toasting.

Some of the characteristics of the end product are shared by both types of product (just battered or battered and breaded): the crisp texture of the external crust, an attractive golden color and a tender, juicy interior.

In both cases, the technological function of the raw batter layer is to create a homogeneous layer that covers the food, which can be raw or cooked, and to adhere to it before and after coagulation—which takes place during the prefrying step—and during final frying. Normally, the pre-fried coated food piece must also withstand freezing temperatures and other processes (packaging and transportation) without cracking or breaking because detachment of any piece of the external layer is a negative quality factor. To achieve these objectives, a whole new generation of ingredients with wide-ranging functionalities is available. They each contribute to the properties of the final system according to their composition, concentration and characteristics. Once fried, the batter layer is transformed into a completely new system: a crust that has to present good acceptability in terms of texture (particularly crispness), flavor and color.

A battery of experimental measurements is available for determining the quality factors required of the external crust, studying changes in them over storage time, or analyzing the effects of variations in the processes or in the formulations. This chapter examines all these measurements, with particular emphasis on certain fundamental concepts and practical aspects that must be remembered during experimental determinations of coated food quality.

## 11.2 CONTROL OF COLOR

### 11.2.1 Some Basic Concepts

Color is directly linked to human eyesight, so instrumental color measurements must be used in conjunction with chromatic perception. Normally, when people attempt to give a precise description of the color of the food, they find that their vocabulary is very limited. Also, humans can discriminate between many colors and are very good at comparing them but, because the human memory for colors is very poor, differences between colors will be assessed well only if all the samples are present or if color cards or references are available for matching. Comparisons with color cards are seldom used because this would require an array of standard colors or color cards for many different foods.

Nonetheless, cards or other reference systems for evaluating the color of a food have advantages. The range of colors covered by specially designed plates generally enables a good match with the sample because they are better fitted to the variations which are expected to be found in the food, such as the yellow-to-gold range for fries (UK English: chips) and chips (UK English: crisps). The form they take varies considerably: strips of plastic or plasticized color cards. Shading or hatching may be added to the standard colors, imitating the visual texture of the samples, and to aid color matching.

Visual assessment demands an excellent knowledge of how and with what to illuminate the sample. For this purpose, a known source of light (i.e., known spectrum distribution) is chosen. The usual choice is the one that is most similar to daylight (illuminant D65 or similar). The detector is the human eye, as the instrument of comparison. Eliminating background contrast effects, or placing "masks" over the food so that only the part to be assessed can be seen, are important. The viewing angle is also important because it must cut out any shine that may appear.

Color measurement methods that use the human eye as the detector have certain drawbacks: the eye could be affected by certain visual defects, variations over time, background and surroundings, or by the perception of shine or shadow. These aspects need to be taken into account in sensory analyses of color.

Depending on the market, coated products are sold with the appearance of a raw food or with golden colors that simulate those of fully fried foods. The former are usually sold with instructions for the final frying that will give them their final golden color. Pallid products resembling a whitish raw batter (their real color when recently prepared) are not very well accepted, so colorings are usually added to give the product a color in the yellow-to-orange range. Foods sold with a fully fried appearance are usually fully cooked and can be finished in conventional or microwave ovens, as well as by the traditional final frying.

The pre-frying stage in the manufacturing process will give the food a slightly golden initial color, depending on the choice of oil. Products coated with tempura-type batters acquire a more yellow color if yellow corn starches or flours are used (Burge 1990) or a golden-brown note through the use of potato starch, or, in general, of systems that combine different types of starches or other ingredients that tend to take part in browning reactions (e.g., reducing sugars from milk solids) (Suderman 1983). Baixauli et al. (2002) established that although the color of the oil used

(sunflower oil) underwent some degree of darkening as the number of times of frying increased, this did not affect the color of the final fried product.

A uniform color is also an important quality factor: spices or minor lumps must not darken during frying and cause a spotted final color.

Coated foods develop a golden color, between yellow and brown, when they are fried. This is a characteristic that consumers normally consider very attractive. During frying, the appearance of dark notes tends to be avoided. These are usually found in areas that have dried out and been overcooked. Black spots from burnt particles adhering to the food as the frying time lengthens are not a desirable feature. A light golden tone is the benchmark color for determining the end of the final frying process.

When instruments are used to measure color, the area to be measured is usually isolated by a window or opening, and shine and shade are eliminated by using the appropriate angle of measurement. Although these "advantages" mean that instrumental measurements are reproducible, they introduce a phase lag between these results and sensory perception that needs to be borne in mind when drawing conclusions.

Instrumental measurements can be considered a quantification of human perception. The usual equipment used for this purpose is a spectrocolorimeter. One disadvantage of colorimeters is that their response is integrated: they provide a single set of tristimulus data for the whole surface measured, whereas the human eye can evaluate a color while "abstracting" it from neighboring zones of other colors, and can therefore ignore small areas of much darker crust when assessing the golden hue of the fried product. Consequently, if there are color variations in that area of the sample, the area has to be reduced to make the colorimeter measurement more accurate.

The chromatic coordinates L*, a* and b* are related to physiologic perception of color: light or dark, red or green and yellow or blue, respectively. It is very easy to obtain these numbers because modern colorimeters have software to calculate these coordinates. However, their interpretation needs to be scientifically based. When the human eye assesses the color of an object, it does not distinguish the quantities of "green–red", "yellow–blue" or "lightness' " separately, but perceives a color that can be described as "light or dark", identified with lightness, "bright or dull", identified with purity or chroma, and the hue, the color itself, in which it will probably not be able to distinguish what quantities of other hues are present. Consequently, analyzing the evolution of the L*, a* and b* values separately often seems unnatural, although most research studies do so.

For instance, it makes no sense to state that "red" or "yellow" has increased from one sample to another (because a rise in the a* or b* values has been registered in the positive zone of these hues) if nobody can see a red or yellow color. It requires the knowledge that a* or b* values close to zero must be interpreted as hues with very little saturation, in other words, very little purity, so they will be grayish tones without any clearly defined color. Generally speaking, this lack of coherence when analyzing results is because color theory is a very broad subject involving many disciplines such as physics, physiology, psychophysics, and statistics, and its measurement and interpretation require a good theoretical foundation, so sometimes the terminology of colorimetry is misused.

When working with color, the most natural way is in terms of the attributes of visual perception: lightness (quantity of light perceived, or the degree of lightness or darkness), hue (the color itself, associated with the predominant wavelength), which is calculated by the following Equation:

$$h_{ab}^* = \arctan (b^*/a^*) \tag{11.1}$$

and chroma (intensity, brightness or purity of the color), which is calculated by the following Equation:

$$C_{ab}^* = (a^{*2} + b^{*2})^{1/2} \tag{11.2}$$

### 11.2.2 The Color of Battered or Breaded Foods

As frying time increases, an evident change in the color of the products takes place: they become darker. On occasion, adding certain ingredients also alters the color of the final products, so being able to measure these differences by using the following calculation can be useful:

$$\Delta E = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2} \tag{11.3}$$

where $\Delta a^* = a^*$ (sample) – $a^*$ (reference), $\Delta b^* = b^*$ (sample) – $b^*$(reference), and $\Delta L^* = L^*$ (sample)–$L^*$(reference), corresponding to the actual sample and a sample taken as reference; these reference values can correspond to a "control" sample or to the initial color before certain processes, depending on the purpose of the study.

Measuring color has made it possible to improve the internal color of cooked batters that were found to be objectionably white, similar to the white of a hard-boiled egg, owing to the addition of a very high-quantity of egg albumen in their formulation. In this case, adding yellow corn flour to the batter gave the cooked coatings more attractive tones (Baker and Scott-Kline 1988).

Starch species (amylomaize, corn, waxy maize, or tapioca) have been found not to have a significant effect on the color development of fried nuggets (Altunakar, Sahin, and Sumnu 2004).

The effect of flour types (addition of 5% soy flour or 5% rice to the batter formulation) on the color of deep-fat fried chicken nuggets was studied by Dogan, Sahin, and Sumnu (2005a); they found that as frying time increased, L* and hue values decreased and the a* value increased. The addition of soy flour gave the nuggets the darkest and most red color; this is related to the high amount of soy flour protein undergoing Maillard reactions. The decrease in L* with frying time was associated with Maillard browning and caramelization at the high frying temperature in a study using chicken nuggets (Ngadi, Li, and Oluka 2007). The rate of the Maillard reaction depends on its chemical environment (such as water activity, pH, and the chemical composition of the food) and reaction temperature.

Smaller breading particle size produced breaded, fried chicken breasts with higher L* and a* values, showing that the use of large-sized particles leads to a reduction in luminosity and a greater reddish component in the color of the fried end products (Maskat and Kerr 2002).

## 11.3 CONTROL OF ADHESION

One of the main quality factors in coated products is a good coating adhesion. Many authors have inspected cooked coated pieces to determine if the outer layer adhered to the substrate or if a gap had formed between the two. A good fried coating adhesion to the substrate in the end product is closely related to the adhesion of the raw batter at the moment it is applied.

Adhesiveness is related to, and heavily dependent on, the nature of the surfaces. For example, if the raw material is frozen, as in the case of fish sticks, a layer of ice results in poor adhesion. The normal practice is to melt this layer with the help of salt. Applying a predust (usually flour-based) also absorbs surface moisture. The same situation arises if the moisture content of the substrate is too high.

The result of poor adhesion is the appearance of voids because there are areas which are bare of any coating. In zones with poor adhesion, the steam generated during frying causes "pillowing" of the coating (appearance of air pockets), or "blow-off" (coating loss in the frying medium). Many works have focused on improving batter adhesion through different predusts (Baker, Darfler, and Vadehra 1972; Yang and Chen 1979) and of gums or proteins in the batter formulations (Usawakesmanee et al. 2004).

The degree of adhesion is related to yield. This means, on one hand, the quantity of batter (greater weight) adhering to a piece of food and, on the other, in the final fried product, the proportion of outer layer to total weight. In tempura-type batters, a thin batter produces a weak, porous coating that is difficult to handle and constitutes a poor barrier against oil absorption and loss of food juices during frying.

In breaded products, the concept of adhesion is slightly different; breadcrumbs or particles will tend to fall off the coated product. This, in turn, is related to the yield of the entire process.

For breaded products, the cooked yield (%) and overall yield (%) have been defined as (Hsia, Smith, and Steffe 1992):

$$\text{Cooked yield (\%)} = \text{CM} \times 100/\text{I} \tag{11.4}$$

$$\%\,\text{overall yield} = \text{S} \times 100/\text{I} \tag{11.5}$$

where CM is the mass of cooked breaded food item, S is the mass of cooked breaded item after shaking (standard sieve and shaking process), and I is the initial mass of the raw food item. The overall percentage yield tries to predict the possible losses in the adhered breaded layer during handling after cooking.

In some works on coated products, the indices mentioned have been used to examine the effects of certain ingredients. Higher fat content has been suggested as a possible cause of higher coating loss during shaking in fried, battered and breaded chicken breasts prepared with different levels of surfactant (Tween 80) and of batter mix to solvent ratios (Maskat and Kerr 2004a). The effects of breadcrumb particle size on coating adhesion have also been studied; coating adhesion was highest in coatings formed from small particle-size breadcrumbs (<250 microns), and lowest in those made from large particles (Maskat and Kerr 2004b).

In batter-coated products, the term “pick-up” is generally used to denote the quantity of batter that has adhered to the piece of food. It is an index that all manufacturers monitor because, as mentioned above, the yield and the quality of the final product depend upon it.

The batter or coating pick-up of the final product is defined as:

$$\text{Batter pick-up (\%)} = (\text{B/B} + \text{S}) \times 100 \tag{11.6}$$

where B is the mass of the batter coating on the food item after final frying, and S is the mass of the food item excluding batter (“peeled”) after final frying (Baixauli et al. 2003).

In this case, the pick-up index expresses the proportion of coating in the final weight of the fried food. These weights include the weight of oil absorbed, and that of both the substrate food and the external crust which will have shed moisture during the frying process.

From the viewpoint of the industrial manufacturer, it may also be of interest to calculate this value after pre-frying. This will give a more accurate picture of the yield of the coating process because it will show which part of the weight of the pre-fried batter-coated food corresponds to the external crust.

Laser scanning confocal microscopy has been used to investigate adhesion of rice flour-based batter to chicken drumsticks (Mukprasirt et al. 2000). The effect of an egg-albumin powder predusting of the chicken pieces, and the effect of combinations of the rice flour with yellow corn flour, oxidized corn starch, methylcellulose, and xanthan gum were evaluated. The batter–substrate interaction, which can be visualized by microscopy, depends on the ingredients. All the samples prepared with the different batter formulations showed good adhesion between batter and substrate. Differences between treatments were observed in the batter layer after 90 days in frozen storage, and could be related to different water-retention properties among the ingredients. The greater or lesser retention of water will be related to the different degrees of damage caused by the growth of ice crystals.

## 11.4 CONTROL OF TEXTURE

### 11.4.1 Some Basic Concepts

The concept of texture in foods covers properties that concern their constitution, nature and structure. The internationally accepted definition is based on an eminently sensory viewpoint: human perception. Texture measurement implies bearing in mind a whole series of actions, stimuli and perceptions on ingesting a foodstuff, or even beforehand, on entering into contact with it and handling it before ingestion. These stimuli, ranging from a crackle or crunch at the first bite and initial break, via the entire stage of chewing and mixing with the saliva, to the feeling of gumminess or chewiness in the mouth and how easy it is to swallow the food, are part of the perception of texture.

The relation that measurements made with instruments bear with the corresponding sensory perceptions of texture is not always direct. For example, in the complex

ingestion processes described, such as chewing, neither the strength of the forces applied nor their speed are uniform because the subject unconsciously adapts them to the stimulus. This varies continually, depending not only on the type of food but also, in the same food, throughout the process. In general, the process of conversion to a bolus implies a gradual reduction in the resistance to chewing. The speed of the jaw movements and the number of chews before swallowing are also variable. The forces exerted are not uniaxial or perpendicular to the piece of food as they are in most of the modern texturometers. Other factors to bear in mind during instrumental measurement are temperature (perception in the mouth is slightly below 37°C); the presence of saliva, which acts as a lubricant and solvent, making chewing easier; the different shapes of teeth etc. These methods have also been joined by those that investigate certain neurophysiologic aspects of swallowing in relation to the texture of the food in question.

In instrumental methods, the tests that are most often applied are the ones known as "imitative tests" using universal texturometers. These texturometers, which have well-defined probes or plungers (known references with regard to their dimensions and the materials from which they are made), make it possible to record the resistance of foodstuffs to compression, shear or, in general, to a combination of forces, depending on the probe employed.

When the sample is of irregular dimensions but its nature allows it to be cut into test samples of known dimensions (normally regular prisms: plugs or blocks), a plunger with a larger surface than that of the sample can be employed, so the forces applied will be those of compression. When subjected to very small deformations, almost all materials show a linear force–deformation response; in these cases, the deformation is directly proportional to the height of the sample and inversely proportional to its area. However, applying greater deformation stresses entails non-elastic or non-recoverable deformation. When the sample is irregular and cannot be cut into reproducible dimensions, the probe of choice is the one smaller than the sample, so the surface in contact is defined by the latter. In this case, the plunger will first compress and then penetrate the sample, and the forces that come into play in this type of test will not be of one single type.

Texturometers have software that makes it easy to record the data and calculate the means. Despite these facilities, it is necessary to know which actions the machine performs, what responses it causes in the food, and which parameters to select as representative of these responses.

The characteristics of a product may not be best described by only one or two parameters, but by the complete curve recorded over the entire test. This profile normally acts as the "digital fingerprint" of the food (Salvador, Sanz, and Fiszman 2002).

It is advisable to know which type of variations between two samples to be assessed may be expected to use the most suitable type of test. For instance, samples and a control sample with the most extreme foreseeable difference (e.g., maximum frying time) could be chosen. In this way, the range of mechanical properties to be described will be known and the probe and conditions can be chosen accordingly.

### 11.4.2 Texture of Battered or Breaded Foods

Crispy, crunchy coated foods, whether fried or baked, add an extra dimension of texture and flavor. In breaded or battered products, one of the main texture characteristics is crispness/crunchiness. It is a primary criterion of sensory quality because it largely determines their acceptability. The crispness that the external layer acquires during frying depends on its initial composition and on the frying temperature and time. During the frying process, it is dehydrated until it provides a crisp texture in the outer part while protecting the tenderness of the inner part (Altunakar, Sahin, and Sumnu 2004).

The greater tendency to employ less time on preparing food at home has led the market to demand ready-to-heat products, normally refrigerated or frozen prepared dishes that people want to heat up in a microwave oven. However, these products tend to have a most undesirably soggy texture (Lenchin and Bell 1985).

The use of susceptor packaging materials in microwave heating is a technology that is gaining ground. Susceptors, which are made of metal, change the heating pattern within the product, making it possible to reach temperatures above the boiling point of water in the microwave oven so that crispy surfaces are achieved (Pszczola 2005).

In this world of multiple sensations that is texture, and especially crispness, many of the instrumental measurements focus on resistance to a force applied by means of a probe; in one way or another, its actions simulate a first bite, generally with the incisors or molars. Many of the mechanical parameters evaluated are indices of the hardness, toughness, and brittleness of the samples which, in turn, are related to crispness measurement but do not represent it fully.

The sandwich-type structure of coated foods presents differences between the layers as regards their mechanical properties, composition and morphology, so it is difficult to determine the relative contribution of each layer to the mechanical behavior of the whole (Luyten, Plijter, and Van Vliet 2004).

Puncture/penetration tests, the Kramer shear cell and the Warner–Bratzler test have been the most commonly used tests to measure the texture of battered fried foods in literature. In recent studies, texture analyses have also been done using acoustic techniques or those related to microstructural data.

#### 11.4.2.1 Puncture/Penetration Tests

The forces involved in puncture/penetration are a combination of tension, compression, and shear; normally, the parameter that best differentiates between the samples is the "point of rupture at maximum force" (Lima and Singh 2001). However, the "fracture force" parameter determined using an 8-mm diameter Magnus Taylor probe has also been used to evaluate the effect of adding certain starches and proteins to rice flour-based batters; the batter samples were not coated onto a food but poured into a Teflon™ mold and deep fried (Mohamed, Hamid, and Hamid 1998). Fiszman's research team (Baixauli et al. 2003; Salvador, Sanz, and Fiszman 2005a) used a 4-mm diameter cylindrical probe for texture measurement of the final fried crust, after removing it from the food, and recorded the maximum force at penetration. The shape of the curves was clearly dependent on the time that had elapsed since frying; a crisp texture was identified as a multi-peak profile of the penetration curve.

Whole samples such as deep-fat fried chicken nuggets are also frequently used for mechanical determinations; the force required to penetrate the samples to 25% of their height was used by Altunakar, Sahin, and Sumnu (2004) as a measure of crispness, while Dogan, Sahin, and Sumnu (2005a) applied the term “fracturability” (or brittleness) to the force at the first significant break during sample penetration by a cone. Mackerel nugget texture measurement has been done on an Instron machine using an 8-mm diameter plunger (Lee, Joaquin, and Lee 2007). In these cases, however, the results of the tests are related more to the general texture of the food measured than to the crispness of the coating.

#### 11.4.2.2 Kramer Shear Cell and Warner–Bratzler Test

A Kramer shear cell was used by Antonova, Mallikarjunan, and Duncan (2003) for breaded chicken nuggets, recording the maximum force peak and the total energy in a test to evaluate the differences arising through different cooking methods, i.e., deep-fat fryer, oven, or microwave oven, and through different holding times after cooking. Shear-press tests have also been applied to measure the instrumental texture of the fried crust of battered onion rings: shear force (maximum force/mass) and toughness (work, which is the area under the loading portion of the curve/mass) were obtained (Du-Ling, Hanna, and Cuppet 1998). An Instron equipped with a Kramer shear cell was used by Usawakesmanee et al. (2004) to measure the texture of fried, battered and breaded potatoes. They determined that fried samples coated with 6% methylcellulose had similar energy at maximum compression load, but lower firmness compared with control samples. Innawong et al. (2006) also used a Kramer shear unit to analyze chicken nuggets fried under a nitrogen atmosphere; peak load, total energy, and energy-to-failure point were the parameters taken to characterize the texture of the fried products.

The Warner–Bratzler test has been used to evaluate the texture of fried pork patties enrobed in a gram-flour based batter (Biswas, Keshri, and Chidanandaiah 2005). Varela, Salvador, and Fiszman (2008) measured the texture of chicken nuggets heated in a conventional oven, in a fryer, and in a microwave oven by a cutting test done with a plastic blade in a TA TXplus texturometer. The force versus displacement curves clearly showed the differences between the samples corresponding to the three types of heating treatment. The fried and oven-heated nuggets showed more peaks, indicating crispy behavior, while the microwaved nuggets showed a smooth curve, revealing a soft, soggy texture.

The number of peaks in the curve obtained with a texturometer has been taken as a measurement of batter crispness in batters by Lee and Lim (2004), who evaluated the addition of normal, high amylose and waxy corn starch and of normal and waxy rice starch to wheat flour batter with the aim of improving the texture, oil uptake, and appearance of fried products. The crispness of the fried battered product was positively correlated with amylose content in starch. Modified starches were also tested, and provided texture improvements in the fried foods.

#### 11.4.2.3 Sound and Ultrasound Approaches to Texture

The pioneering studies of Drake (1963) and Vickers and Bourne (1976) related the perception of crispness to auditory sensations. Several works have recorded the

sound made by foods when compressed or fractured with a texturometer, and others have measured human perception of sound during mastication. However, very few of these studies have been made with coated foods.

Maskat and Kerr (2002) measured acoustic data during mechanical compression of fried, breaded chicken breasts and determined the "jaggedness" of the sound amplitude versus time curves, attempting to determine the differences in crispness according to breading particle size.

Antonova, Mallikarjunan, and Duncan (2003) determined ultrasonic and mechanical parameters of chicken nuggets to investigate their relationships with sensory crispness evaluated by a trained panel. They found significant differences in ultrasonic velocity, transmission loss, peak force, and total energy among nuggets cooked by different methods, and concluded that sensory crispness could be reasonably well predicted by ultrasonic velocity.

Tahnpoonsuk and Hung (1998) used a modified Warner–Bratzler blade to cut breaded fried shrimps through—after different holding times under the heat lamp—and simultaneously recorded the crushing sound with a microphone. These authors found that the crispness loss in a multilayer food did not agree with the changes in mechanical properties. Good correlations were found between sound and force versus displacement curves registered simultaneously with an Acoustic Envelope Detector coupled to a texturometer.

#### 11.4.2.4 Microstructural Approach to Texture

Microstructural studies are a very interesting approach for analyzing the texture of coated fried foods because there is a clear connection between the structure and the mechanical response of food systems. (Fiszman and Salvador 2003).

Battered foods are very complex systems from a structural viewpoint. They tend to contain a wide range of components of very different natures, and the coating and the food substrate undergo substantial changes as a result of frying. Several papers have dealt with this subject in the last decade.

The effects of frying on the microstructure of battered squid rings were analyzed by Llorca et al. (2001). They observed that in the pre-fried products, there was an interconnection between the batter and the squid muscle, whereas in the final fried product the two layers were separate. The same research team also used structure analysis to investigate how some ingredients such as corn flour, salt, or leavening affect the absorption of oil after frying (Llorca et al. 2003). They demonstrated that the generation of gas by a leavening agent increases the oil content because of the voids created.

In a study of breaded fried chicken breasts, scanning electronic microscopy (SEM) demonstrated greater merging between the breadcrumbs and the batter with decreasing breadcrumb particle size (Maskat and Kerr 2004a). Rice flour-based batter formulations (with corn starch or methylcellulose) for chicken drumstick coatings were developed as an alternative to wheat flour-based batters; microstructural analysis has been used to reveal their freezing tolerance (Mukprasirt et al. 2001). The field of microscope observation is probably an area that requires greater attention on the part of researchers of battered or breaded products. Factors such as the degree of adhesion and types of batter-substrate bond could be analyzed in greater depth.

## 11.5 SENSORY ANALYSIS

### 11.5.1 Some Basic Concepts

Sensory tests have been widely applied for evaluating many quality factors in foods. However, the type of information that needs to be taken into account when designing, conducting and analyzing a sensory study with scientific rigor should be remembered. The types of test that are available and the scientific principles on which they are based must be known. The place, the materials used, the samples and the analysis of the results must be carefully planned. Some basic tests used are descriptive sensory analysis and hedonic or affective tests.

Descriptive sensory analysis quantifies the perceived intensities of the sensory characteristics of a product and can provide a complete description of the products. It can constitute the basis for determining the sensory characteristics that are important for acceptability; also, using these methods, process or formulation variables can be related to specific changes in sensory characteristics.

These analyses use limited number of assessors, normally between 8 and 12, who are selected, trained and monitored. They must show skill in perceiving differences within the type of product that will be analyzed regularly. They must also be good at verbalizing their sensory impressions and be able to work as a group. The reliability of each assessor is measured by obtaining repeated replies for each product.

Another characteristic of this method is that it employs descriptors, obtained through consensus, in a sensory language that represents the products to be evaluated. The process generally requires 6 to 10 sessions, each lasting one hour. Also, the descriptor must be defined and, if possible, reference material must be included. Once trained, a taster can act as a measuring instrument. Descriptive sensory analyses are always carried out in the laboratory under standardized conditions.

Hedonic or affective tests attempt to quantify the degree of like or dislike for a product by evaluating the response (reaction, preference or acceptance) of real or potential consumers of a product. Unlike analytical methods, which are carried out with chosen, trained assessors, affective tests are conducted with a large group (usually >100) of target consumers of the product. The larger size of the affective test panel is due to the high variability of individual preferences and the consequent need to ensure its statistical power and sensitivity. Scales (normally 9-point scales) are used to obtain information from respondents on the degree of like or dislike. They are balanced for liking, with a centered neutral category, and attempt to produce scale point labels with adverbs that represent psychologically equal steps or changes in hedonic tone (Lawless and Heymann 1998).

The choice of a preference test or an acceptability test depends on the objectives pursued. If the aim is to compare one product with another, a preference (choice) test is appropriate, taking preference to mean a predilection or favorable disposition towards a sample when compared with another and not necessarily an indication that the product being tested enjoys high acceptability. If what is sought is the level of acceptance of various samples, the appropriate test is one of acceptability (measurement), where acceptability or acceptance is defined as the individual or collective act of accepting a product for consumption.

Various factors can be taken into account when choosing the consumers: the segment of the population that the product targets; how often the product is used;

age, sex, or the socioeconomic bracket of consumers. The size of the sample population for the test is calculated on the basis of the following factors, among others: size and heterogeneity of the population, whether the results are intended to serve as guidelines or to be definitive, the number of characteristics to be estimated, and the available financial, human, time and sampling resources.

Sensory acceptability tests can be conducted in the laboratory, in centralized premises, in the home and in mobile units. The first two are used very frequently because access is easy, the test conditions can be tightly controlled, and the results can be analyzed swiftly. Centralized locations are the most habitual in market research. It is recommended that the number of samples to be tested should not exceed four, and the number of consumers required is greater than in the tests which are conducted in a laboratory. Tests carried out at home are very valuable for obtaining information on product preparation, the attitudes and opinions of different family members and other questions in connection with overall acceptability (convenience, packaging, cost). The recommended number of samples to be evaluated at home is no more than two because more time is required for testing them.

### 11.5.2 Sensory Analysis of Battered or Breaded Foods

Many of the sensory parameters that are determined in coated fried products refer to factors concerning the external appearance of the fried crust which are difficult to quantify by instrumental methods:

- bubbles
- smoothness
- integrity (wholeness)
- color
- uniformity of color
- overall appearance
- coating adhesion
- weepage (oil exudation).

Others refer to the quality properties of the product when it is eaten:

- crispness/crunchiness of coating
- adherence of coating
- greasiness, oiliness
- juiciness of the substrate
- tenderness of the substrate
- rancid flavor
- interface.

Attributes that are applicable to any other food can also be evaluated:

- flavor
- taste
- texture
- hardness, softness
- firmness

- moistness
- overall acceptability
- overall desirability

Some examples of sensory analyses include the studies described below.

A panel of 40 persons was used by Ballard, Mallikarjunan, and Duncan (2007) to study if there were any differences between fried chicken nugget samples when nitrogen gas or steam was used as the pressure source for frying; 9-point intensity scales were used for soggy/very crisp, not juicy/very juicy, no chicken flavor/high chicken flavor, and a 9-point hedonic scale was used for dislike extremely/like extremely, or overall liking for the samples.

Specially trained panels are less frequently used. One example is the eight-member panel trained to assess crispness, defined as the force and noise level at which a product breaks or fractures (rather than deforms) when chewed with the molar teeth, in the study of Antonova, Mallikarjunan, and Duncan (2004). In this study, the panel was used to evaluate breaded fried chicken and successfully distinguished the differences due to the use of different cooking methods.

Variation in texture due to different moisture levels in the formulations, different combinations of moisture-releasing vegetables and added water, and different milk–water combinations in nuggets were evaluated by a sensory panel for firmness, moistness and overall desirability (Lee, Joaquin, and Lee 2007). The main ingredients of the nuggets included mackerel mince, mild cheddar cheese, and hydrated textured soy protein concentrate. Milk proved more effective than water in achieving moistness and a tender texture.

A consumer study was used to assess the acceptability of fried batter-coated squid prepared by a method that reduces their fat content, examining the influence of imparting favorable nutritional information (nil industrial fats content and less absorption of frying oil) or of a period of familiarization (consumption in the consumers' own homes) on the sensory acceptability of fried batter-coated squid (Salvador, Hough, and Fiszman 2005b); in this study, consumers evaluated appearance, crispness, and thickness of the crust.

In another study, the characteristics of stored emulsion and restructured buffalo meat nuggets were compared. In spite of an initially higher overall acceptance of the stored emulsion nuggets, panelists rated them considerably lower than the restructured nuggets during subsequent storage (Rajendran, Anjaneyulu, and Kondaiah 2006).

## 11.6 CONTROL OF OIL UPTAKE IN BATTERED AND FRIED FOODS

One of the main problems associated with batter-coated food consumption is the considerable amount of oil absorbed during the pre-frying and frying operations. This fact has prompted studies of ways to lower their oil content. Many factors affect oil uptake, including oil quality, frying temperature and duration, cooling period, and the shape, composition, and porosity of the product. Apart from these, several ingredients have been proved to reduce the amount of oil absorbed by the food in fried battered products.

Among the different gums employed as fat barriers, the use of the cellulose ethers MC and HPMC, which possess the unique property of reversible thermal gelation, has been more widely investigated and reported than that of other gums. In contact with hot oil, the MC or HPMC in the batter gels to form a film. Together with their high water-retention capacity, this protects against moisture loss and the entry of oil during the frying process (Balasubramaniam et al. 1997; Mallikarjunan, et al. 1997; Meyers and Conklin 1990). The employment of MC and HPMC films has been shown to be effective in a wide range of applications such as chicken nuggets (Meyers and Conklin 1990), mushroom, chicken breast strips and codfish fillets (Ang 1993), coated chicken balls (Balasubramaniam, et al. 1997), mashed potato balls (Mallikarjunan, et al. 1997) and chicken strips (Holownia et al. 2000).

Sanz, Salvador, and Fiszman (2004) found that raising the MC concentration in a batter from 1% to 2% led to lower oil absorption and a greater moisture reduction in the crust of batter-coated squid rings after pre-frying for 30 s and after the final frying subsequent to freezing. At all three concentrations studied, the effectiveness of the barrier was more evident after the 30 s pre-frying.

As well as adding hydrocolloids to the batter mix, another possibility that has been tested is to form an edible film around the pieces of food by dipping them in a solution of MC or HPMC. The influence of applying HPMC and MC as a film before breading or of adding these substances to the breading formulation to reduce the amount of oil absorbed by the crust has been evaluated in marinated chicken strips (Holownia et al. 2000); the most efficient method was to add the dry hydrocolloid to the breading formulation. In this work, application as a film before breading did not reduce the amount of oil absorbed by the crust, but did reduce its moisture; this was associated with an inhibition of the migration of moisture from the substrate into the crust. Applying the film after breading was rejected owing to adhesion problems. A film composed of gelatin and starches reduced oil absorption upon frying by up to about 50% according to Olson and Zoss (1985).

Other gel-forming hydrocolloids which have been employed as barriers against fat absorption are gellan gum and pectin. Gellan gum—the anionic linear heteropolysaccharide produced by *Pseudomonas elodea*—can be applied as a hot solution: the food is dipped into the solution and the film forms as it cools. Another possibility is to dip the food into a cold gellan solution: gelation takes place after ions such as $Na^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $K^{+}$ have been added (Duxbury 1993). Gellan gum has also been added with calcium chloride to the dry ingredient mixture of batters for chicken, fish, cheese and vegetables, resulting in low oil absorption and the development of appropriate crispness; and gellan solutions have been used to coat the crumbs used for breading; the use of these rather than conventional breading crumbs achieved a final product with excellent crispness and lower oil absorption (Chalupa and Sanderson 1994). As regards the use of pectin, this substance gels in contact with calcium. When $Ca^{2+}$ is added to the breading, and the batter-coated and breaded food is treated with a solution of calcium-reactive pectin, a hydrophilic film that reduces the absorption of oil forms during the reaction between the $Ca^{2+}$ and the pectin. The level of $Ca^{2+}$ added to the breading has to be sufficient for efficient reaction with the pectin (Gerrish, Higgins, and Kresl 1997).

Adding rice starch to the batter has also been studied. Shih and Daigle (1999) used pre-gelatinized and modified rice starches to achieve reduction of the oil uptake

by the batter without affecting the eating properties of the batter-coated product. Replacing a portion of the wheat-corn flour in batters with rice flour or soy flour has been recommended for reducing the oil content in chicken nuggets (Dogan, Sahin, and Sumnu 2005a).

The replacement of part of the wheat flour with corn flour significantly decreased the oil uptake in battered squid rings in a study by Llorca et al. (2003). These authors also reported that the use of a leavening agent significantly increased the fat content: the generation of gas cells where oil can easily lodge was the most important event that they observed by SEM.

Adding steam jet-cooked barley flour to frying batters increased batter pickup and viscosity, and reduced the moisture loss of the fried batters. These combined effects significantly lowered the oil uptake (Lee and Inglett 2006).

Some proteins such as soy protein isolate (SPI), egg albumen (EA) or whey protein isolate (WPI) have been studied with the aim of reducing oil absorption in chicken nuggets. EA reduced the oil content significantly, but yielded softer products. WPI-added batters provided the crunchiest product and also significantly reduced the oil content of the fried nuggets (Dogan, Sahin, and Sumnu 2005b). A soy protein film coating has also been applied to reduce fat transfer in deep-fried foods during frying; a solution of 10% SPI with 0.05% gellan gum as plasticizer was recommended as suitable for coatings (Rayner et al. 2000).

## 11.7 CONCLUSIONS

Coatings produce a crisp, well-colored exterior that acts as a shield to preserve the moisture and flavor of the coated food. The formulations employed to achieve this objective have evolved into increasingly complex and sophisticated systems. Companies should consider trying new ingredients and methods, or trying old ones in new applications. New ingredients, innovative presentations, and extra dimensions of texture open up a whole world of opportunities, while healthier dietary trends are making food companies and coating suppliers review their formulations to fall more into step with the times by reformulating, redesigning and redefining food coating systems. The result is a new generation of enhanced breading/batter systems which are friendlier to processors and consumers. The new challenges are whole-grain breadings, oven-usable or microwaveable products, coatings that will hold their texture for extended holding times, coatings with reduced fat, sodium, and carbohydrate contents, or more coated vegetable and meat substitute products. The wide range of possibilities makes it necessary to employ increasingly strict processes and controls, if necessary by developing new methods that will determine the factors which define the quality of the end product accurately. It is a vital necessity to discover these methods and apply them appropriately

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# 12 Industrial Frying

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## CONTENTS



## 12.1 INTRODUCTION

Food frying has been used by man since ancient times. It was found to be a rapid way to prepare food. Fried foods are tasty because of the pleasant feeling produced by the oil absorbed in the fried food. The absorbed oil also increases the salivation process, which helps the release of oil soluble flavors from the fried food, making it very appealing to the taster. Fried food is particularly popular in USA, Canada, Mexico, Central America, South America, the Caribbean Europe, India, China, Japan, and Malaysia.

Technology of frying has vastly improved through research over the years. Frying is no longer the technique used in kitchen frying. The industry has evolved into a

large-scale industrial frying processes that can fry thousands of pounds of product per hour. This can then be packaged and shipped directly to stores and also to warehouses for distribution. Besides fried salty snacks, products like coated products, and par-fried products (with or without seasoning) were introduced to the market in the last 50–60 years. Innovation in packaging technology has helped the industrial fried products to maintain their quality over an extended period. This has allowed inter-continental shipment of various fried products without sacrificing the shelf-life of the products.

In frying, food is dehydrated by using the thermal energy from a bed of hot oil. The oil is heated by electrical or gas heating. The frying process can be divided into three major categories: home frying, restaurant or food service frying, and industrial frying. This chapter focuses on industrial frying, discussing the various aspects of processes and critical control areas.

## 12.2 SIGNIFICANCE OF INDUSTRIAL FRYING IN THE FOOD INDUSTRY

Industrial frying has become a major segment of the overall food industry. Production of various fully fried, microwavable and par-fried products has grown. These products are used by consumers as well as restaurants and food services.

The most commonly known industrial fried products are potato chips (plain or seasoned), tortilla chips, corn chips, fabricated products, extruded corn products (seasoned (salty) and coated (sweet)) batter-coated products, par-fried products (e.g., French fries, fish, chicken, cheese, vegetables) and fried nuts (salty, seasoned or coated (sweet)).

Potato chips and tortilla chips are household names for salty snacks in USA. Potato chips and various other potato products are common in Europe and UK. Corn products are more common in USA, Canada and Mexico, but not in Europe or elsewhere. Fabricated products are produced from pellets or from sheeted material made from pre-processed and formulated mixture of ingredients. Products made from formulated sheets as well as from the pellets are sold as salted as well as seasoned. Most well-known products of this category in the USA are Pringles® made by Procter & Gamble Company, and Lay's Stax® made by Frito Lay.

Batter-coated fried foods include a wide variety of products, such as coated shrimp, coated fish, corn dogs, coated potatoes, coated French fries, fried chicken and many other popular restaurant items. These products are also packaged to be sold in supermarkets for consumer use. Flash frying has been used to deliver good stable batter-coated products. These products are manufactured on large scales and distributed in a frozen state. The frozen products are removed from the freezer, fried without thawing and served immediately for consumption.

Fried meat, poultry and seafood products, such as chicken-fried steaks, batter-coated chicken, batter-coated fish fillet and batter-coated shrimp, are manufactured on large scales and distributed to restaurants in the frozen state. These products, especially the par-fried frozen poultry and seafood products, are also shipped overseas. Frying of whole birds, such as turkey or chicken, is gaining popularity in the USA and Europe.

Par-frying of French fries has grown to become multi-billion dollar business since its inception in the 1950s.

The sales of salty snack food in 2007 were $25.7 billion in the USA (Table 12.1) and total worldwide sales were more than double of figure.

Sales of potato chips are the highest in the snack food industry. The next big seller is tortilla chips. The net increase in salty snack food sales in USA was 3.7% more than the previous year. The European snack food market is very large, but it is difficult to get sales information. Data can be obtained from the European Snack Food Association.

Other industrially fried products of significant importance in terms of production volumes are French fries and breaded fish sticks and shrimp. The Netherlands, Canada, Japan and USA produce and export most of the frozen par-fried French fries. The total production of French fries was about 5.92 billion metric tons in year 2000.

From the above discussion, one can appreciate the size of the snack food business. The low-oil and no-oil category of snack foods that began to flourish in the late 1980s through the 1990s have shown a significant decline in their demand. The fat-free product made from olean (Olestra) has also shown a significant decline in volume since its introduction and its initial growth. The latest challenge in the fried food industry is to produce products with low or no *trans* fats. This requires oils that are not hydrogenated but which are stable under frying conditions.

The technology in the frying industry has evolved greatly from the early days of kitchen frying to highly automated industrial frying. Innovative packaging techniques have helped the industry to deliver products with longer shelf-life. Frying equipment development has also allowed the industry to manufacture products with specific traits

**TABLE 12.1**
**Sales of Salty Snack Food in USA in 2007**

| Segment | Dollar sales ($ millions) | % Change from previous year |
|---|---|---|
| Potato chips[a] | 6,393.7 | +0.9 |
| Tortilla chips | 4,866.9 | +5.4 |
| Corn snacks | 835.3 | +1.9 |
| Pretzels | 1,334.3 | +6.8 |
| Microwave popcorn | 1,276.9 | −2.3 |
| RTE Popcorn | 468.9 | +5.2 |
| Snack nuts<br>Seeds<br>Corn nuts | 2,861.0 | +3.5 |
| Meat snacks | 2,779.0 | +6.7 |
| Pork rinds | 607.6 | +8.1 |
| Cheese snacks | 1256.5 | −1.4 |
| Variety packs | 371.6 | +6.3 |
| Other snacks | 2,662.1 | +13.7 |
| Total salty snacks | 25,659.8 | +13.7 |

[a] Includes baked potatoes.

that were not previously possible. There has been significant improvement in the oil heating techniques to obtain longer life for frying oil.

## 12.3 EVOLUTION OF THE FRYING INDUSTRY INTO DIVERSE PRODUCTS

A great deal of evolution has taken place in frying industry from the early days of frying potato chips in kettles. The fryers are larger and more sophisticated in terms of product feed, internal construction, oil temperature control and distribution. They are complicated in design, but deliver large volumes of product with high quality.

To preserve oil quality in the fryer, the oil volume in the frying system has also been reduced in many designs.

Batch fryers have been traditionally used to produce smaller volumes and harder texture in the fried chips. New continuous fryers have successfully duplicated the harder texture of the kettle-fried chips, and at a higher production rate.

Continuous fryers with very specialized design of the frying bed have been developed to fry preformed or fabricated chips as well as chicken/fish nuggets or patties. These products require variable fry time. Therefore, these fryer belts are designed differently from the traditional snack food fryers. Some of these fryers show a high degree of oil degradation because of high oil turn over time. Figure 12.1 shows the Heat Wave fryer from Heat & Control Company. In this fryer, the individual product pieces travel in miniature frying baskets which are integral part of the fryer conveyor. Hot frying oil gently cascades over the product being fried. This fryer has several advantages over the conventional fryers that are used for frying formed products. Because of the gentle treatment of the oil, significantly lower oil oxidation is expected. However, several complaints regarding excessive oil degradation were received by the manufacturer since the introduction of this type of fryer. Heat & Control Company have reported some progress in resolving this issue.



**FIGURE 12.1** Heat wave fryer (Courtesy of Heat & Control Company).

Par-fried products, such as French fries, potato nuggets, chicken, and chicken fried steaks, are frozen immediately after frying and stored at –5°F (–20.6°C) to –10°F (–23.3°C). The product is distributed in freezer trucks. These products are fried directly from "freezer to fryer" without being thawed and served immediately at the restaurants, food services and even at home. These products have the great advantage of convenience and reduced cost. Products, such as par-fried French fries, chicken and coated vegetables require shortening with fairly high level of solids. This can be achieved through the standard hydrogenation process, fractionation process or the trans-esterification process as it is done in most countries. Batter-coated fish-fillet is fried in lightly hydrogenated oil or non-hydrogenated oil. The storage temperature of –5°F (–20.6°C) to –10°F (–23.3°C) helps protect the oil from rapid oxidation. This also allows the food processors to use non-hydrogenated oils.

The USA, Canada and the Netherlands are the major producers and exporters of frozen French fries. According to the Department of Commerce, US Census Bureau, Foreign Trade Statistics, the USA exported frozen French fries worth nearly $316 million in 2002. The other par-fried frozen products are fish sticks, breaded shrimp and par-fried chicken.

During the 1980s, consumers started to ask for reduced fat in food, including snack food. The demand for the reduced-fat and no-fat product was rising during the 1990s. The demand has tapered-off and consumers are not demanding no-fat snack food as previously. This might be due to the fact that the no-fat snack food did not have the same palatability as the standard or low-oil snack food products. There is still some demand for low-oil snack food.

According to the USA Food & Drug Administration, the food can be called "reduced fat" if the oil content is reduced by 33.3% of the original (standard) level.

In the production of low-oil potato chips, potato chips are partially dehydrated in the fryer to a moisture content of 8–12%. Then, they pass through a de-oiler, where some of the oil from the surface of the product is blown off by high-velocity steam, air or nitrogen at high temperature. The cooking of the chips is completed in the de-oiler. The moisture content of the finished product is about 1.5%. The finished product contains one-third less oil than conventional potato chips. The product is handled in the same manner as regular potato chips.

## 12.4 TYPES OF INDUSTRIAL FRYERS

Industrial fryers can be classified into batch fryers (kettle fryers, vacuum fryers) and continuous fryers.

### 12.4.1 Batch Fryers

Batch fryers include kettle fryers and vacuum fryers.

#### 12.4.1.1 Kettles

These fryers resemble the so-called "restaurant fryers", except they are much larger, and capable of frying several hundred pounds of product per batch. Figure 12.2 shows a typical kettle fryer. These fryers are used for frying specialty-type products such

as kettle fried Hawaiian style potato chips. The product has a distinct hard texture, appearance and flavor.

Oil is placed in a large pan with a typical capacity of 300–400 US gallons. The oil is heated by gas burners, located under the pan. This method of heating the oil is known as the "direct heating" system. In certain installations, oil is heated in an external heat exchanger. In this case, oil is continuously taken out of the fryer, circulated through an external oil heater and returned back into the fryer pan. This is called the "indirect heating" system. External oil heaters can be steam-heated or gas-fired. The steam heat exchangers are generally the shell and tube type, with the oil passing through the tubes and steam on the jacket side. Moderate-pressure steam (180–200 psi) is used. Gas-fired heaters are of different designs. In some of these heaters, the oil in tubes is exposed directly in the path of the flue gas. Others use the hot flue gas from the burners to heat air, which in turn heats the oil in tubes. A level control maintains the oil level and a temperature control device maintains the oil temperature in the pan.

In batch frying, oil temperature is allowed to reach the desired steady state condition (Typically 304–306°F or 151–152°C). Then, a specified amount of raw product is added into the pan. The oil temperature drops sharply to 250–260°F (121–127°C) with the addition of raw material. The temperature then recovers as more moisture is removed from the product, and the product approaches the final moisture content. During frying, the product is stirred with a manual stirrer or an automatic stirrer. The oil temperature generally reaches approximately 300°F (149°C) when the final moisture target is reached. The product is taken out of the kettle. The oil temperature continues to rise and fresh product feed comes in when the oil reaches 304–306°F (151–152°C). The product is removed from the fryer with a take-out conveyor. The product can be centrifuged to remove the excess oil on the surface of the product. Finally, the product is salted or seasoned and packaged.

#### 12.4.1.2 Vacuum Fryers

Vacuum fryers are used to fry fruits or vegetables. It is important to retain the original product color with minimum browning. These fryers generally have low



**FIGURE 12.2** Batch fryer (kettle) (Courtesy of Heat & Control Company).

production capacity. They are very expensive. Mostly batch vacuum fryers are used. Continuous vacuum fryers are difficult to build and operate. They are also very expensive and rarely used.

Vacuum batch fryers have several distinctive features. The fryer is operated at a pressure of $\leq 100$ mmHg and frying is conducted at approximately 250°F (121.1°C). The food dehydrates at this temperature under the vacuum. In vacuum frying, the oil is heated through an external oil heater. The food is placed in a basket. The basket is placed in the vacuum chamber above the surface of the oil. The door on the vacuum frying chamber is closed, locked and vacuum is applied. The basket is lowered into the hot oil at an approximate temperature of 250°F (121.1°C) when the vacuum in the chamber reaches $\leq 100$ mmHg pressure. The oil temperature drops immediately when the food is immersed (as described in a batch fryer). The oil is circulated continuously through an external heater. The oil regains the temperature when the moisture content of the product reaches the pre-determined value. After frying, the vacuum in the fryer is broken slowly. This is preferably done using nitrogen instead of air to protect the oil from oxidation. The door on the frying chamber is opened and the product basket removed. The excess oil is allowed to drain and the product is cooled before packaging.

### 12.4.2 Continuous Fryers

Continuous fryers are used for large-scale production of fried snacks. They have different designs such as straight-through frying pan, horse-shoe design and multi-zone fryer.

#### 12.4.2.1 Straight-through Fryer

In the straight-through frying pan, product is fried in hot oil and heated in a straight pan with temperature and level controls. The product is fed into the fryer at one end and the fried product is removed from the opposite end by a take-out conveyor. The internal construction of the fryer varies greatly with the type of product fried. As in batch fryers, oil in a continuous fryer is heated by direct or indirect oil heaters (Figure 12.3 and Figure 12.4).

#### 12.4.2.2 Horse-shoe Fryer

The fryer pan is made in the shape of a horse-shoe. The product enters at one end and is taken out at the other end of the horse-shoe. The mode of oil heating, product feed and take-out are similar to that in the straight-through fryer.

#### 12.4.2.3 Multi-zone Fryer

Multi-zone fryers have become popular because they can maintain a more uniform oil temperature and improved controlled dehydration of the product. The oil is heated in an external heater and is pumped at several pre-determined locations of the frying pan (Figure 12.5).

Multi-zone fryers may exhibit rapid oil degradation compared with that in a conventional straight-through fryer of similar capacity because the average oil temperature in this fryer is maintained higher throughout the length of the fryer compared with that

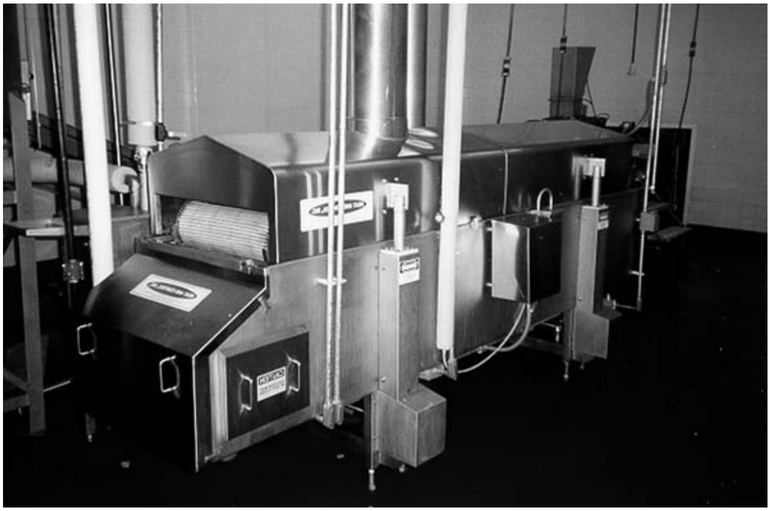


**FIGURE 12.3** Direct fired fryer (Courtesy of Heat & Control Company).

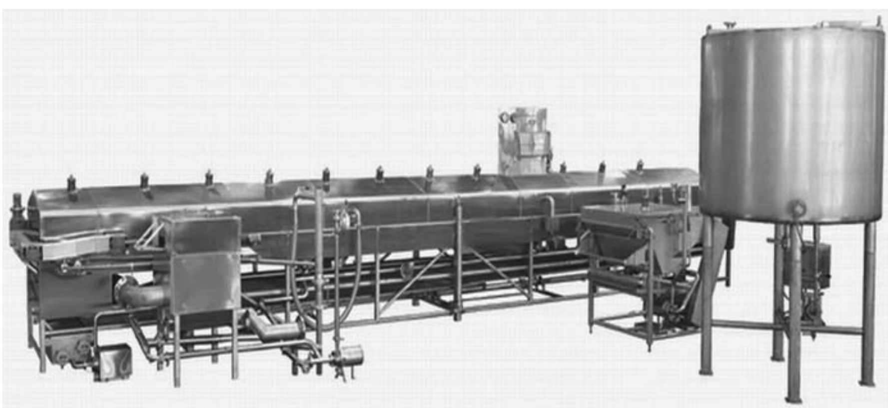


**FIGURE 12.4** Indirect heated fryer (Courtesy of Heat & Control Company).

in a straight through fryer. In addition, without careful designing, the multi-zone fryer tends to hold a higher volume of oil than a straight-through fryer of equal capacity. This increases the oil turnover time, which causes higher oil degradation.

## 12.5 CRITERIA FOR FRYER SELECTION

A fryer selected for frying a given product must meet all the requirements to deliver the desired product attributes. At the outset, it may appear to someone unfamiliar with industrial frying that a food can be fried in all types of fryers. In reality, the fryer is selected on the basis of the type of product to be fried, physical property of the food to be fried, i.e., whether the food floats or sinks or expands in the fryer, and the volume or rate of production needed.



**FIGURE 12.5** Multi-zone fryer (Courtesy of Heat & Control Company).

Snack food products vary considerably in their physical behavior during frying. For example, many snack products such as potato chips, tempura-coated products and certain other coated products tend to float in the fryer and, therefore, must be submerged in the oil with a mechanical submerger. Certain products such as donuts float on the oil surface and the frying is conducted in this fashion. Therefore, they need different designs for the feed belts. Chicken fried steaks, French fries, and nuts sink in the fryer. These products need special design feed belts. Products like pellets expand many folds in the fryer and must be fully submerged. Therefore, fryer volume is critical for accommodating large volume of product. It is important to know whether the food product is going to sink or float in the fryer. For "semi-buoyant" products, the fryer needs only a main (bottom) conveyor if the product sinks and a submerger conveyor if the product is buoyant. Submerger conveyor keeps the product submerged in the oil during frying while the main conveyor carries the product through the fryer. For products that change buoyancy during frying, the fryers must have a main and submerger conveyor.

There are other important criteria that must be considered to design a suitable fryer for the process, as listed below.

- Finished product characteristics, such as appearance, texture, and moisture content.
- Required production capacity.
- Required heat load (also referred to as thermal load), which depends on the moisture content of the feed and the finished product at the required production capacity.
- Desired oil turnover time, which must be minimized to minimize oil degradation during frying.
- Required accessories for the fryer feed, frying and product take out.
- Oil filtration system to remove fines from the fryer oil.
- Ease of fryer sanitation.
- Ease of maintenance of the system.

- Emission control for the fryer exhaust as required in certain cities or states.
- Mode of oil heating (direct or indirect)
- Technical support readily available from the fryer manufacturer.

## 12.6 COMPONENTS IN AN INDUSTRIAL FRYING SYSTEM

The fryer is the center piece in an industrial frying system. There are several other integral and peripheral components that are required to complete the design of an industrial frying system, as listed below. This includes:

- Potato washing, peeling, slicing and slice washing for potato chip fryer
- Corn cooking, washing, masa preparation, sheeter, cutter, for tortilla chip fryer
- Corn cooking, washing, masa preparation, and extruder for corn chip process
- Blending of grains or ground ingredients, hydration system and extruder for various extruded products
- Conveyors for product feed to the fryer and take out.
- Salt applicator.
- Seasoning applicator.
- Toasting oven for tortilla chips.
- Equilibrator (cooler) for tortilla chips.
- Extruder for the extruded products.
- Stirrers for batch fryers.
- Optical sorters for product color monitoring.
- Oil receiving and storage system.
- Oil filter.
- Oil recirculation pump and piping.
- Oil heating system for direct and indirect heated fryers.
- Product conveying system to the filling machines.
- Conveyors and submerger in the fryer.
- Specially designed conveyor that dredges the frying pan to remove the accumulated solids or sludge from coated products.
- Paddle wheels for potato chip fryer.
- Metal detectors.
- Filling/packaging machine.
- Nitrogen flush (if used) at the filling machine.
- Modified atmosphere packaging system for certain products.
- Oil temperature controller.
- Oil level controller.
- Process alarm for any process upset.
- Fire-suppression device.

Thus, one can see why the fryer is the centerpiece for the entire frying system, and the peripheral units provide the capability for the fryer to make the appropriate product.

## 12.7 EXAMPLES FOR FRYING PROCESSES

Some of the individual processes for making fried products are described below.

### 12.7.1 Continuous Potato Chip Process

In the potato chip process, potatoes are washed with clean, cold water to remove the mud and sand from the surface. It is important to remove these extraneous materials because they adversely affect product and oil quality during the process. The clay or mud on the potatoes contains calcium and magnesium compounds which can react with the free fatty acids in the fryer oil, producing calcium and or magnesium soap. These soaps accelerate the formation of free fatty acids in the fryer oil as well as accelerating oxidative degradation. Rocks and stones are removed in a de-stoner. Their presence can damage the slicer blades, make them blunt or break them. A mechanical or a steam peeler is used to remove most of the peel from the surface of the potatoes. Then, the potatoes pass through an inspection table where the defective potatoes are manually removed and all large tubers are cut into smaller pieces. Peeled potatoes are held submerged in a bed of cold water before they pass through the slicer. This operation protects the potato surface from enzymatic browning. The desired slice thickness for the slices is accomplished in a high-speed slicer. Water is added into the slicer along with the potatoes (Figure 12.6). The surface starch from the slices is removed in a washer to minimize darkening of the oil due to charring of the starch. This also protects the potato chips from turning brown and developing



**FIGURE 12.6** High-speed potato slicer (Courtesy of Urschel Company).

a burnt flavor. There are different types of washers, such as drum washers and high-speed washers. In drum washers, the slices are washed in a perforated drum, rotating over a bed of water which is continuously replenished. High-speed washers are becoming more common because of their higher efficiency.

A high-speed draining cum feed belt feeds the slices to the fryer in a single layer. This minimizes the amount of water entering the fryer along with the feed, and provides better frying in the free-fry zone. This also reduces formation of clusters where several chips form clumps. In the free-frying zone, potato slices come in contact with the highest oil temperature (360°F or 182.2°C) that produces maximum initial dehydration. The slices (chips) then enter a zone where their forward flow along the length of the fryer is controlled by a set of paddle wheels. The rate of rotation (RPM) and the inter-meshing of the adjoining paddles are set carefully by the fryer manufacturer. The chips then pass through a zone where a set of submergers holds the product under the oil surface. This completes the last dehydration of the product. A take-out conveyor carries the fried chips out of the fryer. These conveyors are specially designed to drain the excess oil from the chips. The potato chip fryer is shown in Figure 12.7. The total fry-time is about 2 min 45 s to 3 min. Moisture in the fried chips is about 1.5%. At the end of the fryer, the oil temperature drops by 40°F (22.2°C) to 50°F (27.8°C) compared with the inlet temperature of 360°F (182.2°C).

The oil leaving the fryer passes through a filter screen and is pumped though an external heat exchanger to heat the oil back to 360°F or 182.2°C. The oil at the product exit end leaves the fryer, goes through a filter, is re-circulated through



**FIGURE 12.7** Potato chip fryer (Courtesy of Heat & Control Company).

an external heater and fed back to the fryer at the product feed end. The heated oil enters the fryer at the product inlet end through a manifold that distributes the oil evenly across the width of the fryer pan. Fresh oil is added to compensate for the oil carried out by the product and maintain proper oil level in the fryer. The fresh oil make-up location varies with the fryer design.

The salt applicator is normally situated near the discharge end of the fryer, but precautions are taken to prevent the salt being blown into the fryer oil due to the draft created by the air flow system at the plant. Salt in the fryer oil can degrade the oil rapidly. Seasoning is applied in a tumbler. Most seasonings come pre-blended with salt. Therefore, the seasoned products do not require additional salt. The finished product is packaged mostly in metallized bags with nitrogen flush for long shelf-life. The maximum oxygen content in the bags is $<2\%$. The seals are made by jaws that are horizontal or vertical. Generally, the horizontal jaw is preferred. The bags are packaged in cases and sent to the warehouse for distribution. Product quality is checked after frying, after applying the seasoning, and after it is filled in the bags. Quality of fryer oil is checked regularly.

### 12.7.2 Continuous Tortilla Chip Frying System

Corn is the main ingredient in tortilla chips. In tortilla chip production, freshly cooked corn is ground-up or corn flour (masica) is mixed with water to make masa.

In tortilla chip production, corn is cooked in a vat or in a continuous cooker with a certain amount of lime (calcium hydroxide) to soften the outer shell of the corn. This also adds some flavor to the product. A water-washing step removes the excess lime from the surface of the cooked corn. The corn is ground in a stone (or stainless steel) grinder (mill) to make dough called the masa. The degree of grinding is carefully controlled to obtain the right masa characteristics. Additional water is added to the mill. The water content of the final masa is approximately 50%. The masa is then sheeted and cut to a specific size and shape.

The raw chips are passed through a gas-fired toaster oven, where the temperature is about 640°F (338°C). The chips lose some moisture and also develop some toast-points on the surface. This gives the pleasant toasted flavor in the finished product. The degree of toasting is carefully controlled. Over-toasting can produce a burnt flavor in the product. On the other hand, under-toasted chips develop lower corn flavor after frying. The chips from the toaster-oven then pass through an equilibrator. This is a chamber with open sides where the chips pass through a series of special conveyor belts. This is done to achieve an even distribution of moisture in the chips and more uniform color and texture of the chips. Moisture of the chips at this stage is about 40% for masa made from cooked corn and 30–35% for the chips made from dry corn masica. Temperature of the chips reaches below 100°F (38°C).

The product is then fried in a horseshoe-shape fryer or a straight-through fryer. The frying oil temperature is approximately 350°F (177°C). The delta-T is 10°F (5.6°C). The value of delta-T in this case is much lower than in potato chip process because of the lower moisture removal required by the oil. Frying time is $<1$ minute, which is very short compared with potato chips frying. The fried chips contain

approximately 1% moisture. The product removal, salting and seasoning application techniques are similar to those in the potato chips frying operation. The seasoned product is filled mostly in clear bags. Metallized bags with nitrogen flush are used by some manufacturers.

### 12.7.3 Frying of Extruded Products

Various fried extruded products are manufactured. Like other products, these are also seasoned and packaged for distribution. One of the popular products is extruded corn chips, which are sold primarily in North America. This product is made from the cooked corn or from masica and then extruded through extruders. The product is added directly into the fryer and is generally fried at a higher temperature 415°F (213°C) than tortilla chips or potato chips. These fryers have shallow frying pans. Some extruded and fried products are coated with seasoning in oil slurry.

### 12.7.4 Frying of Coated Products

Coated products are batter coated and par-fried. The typical fryer oil temperature for most coated products is 380°F (193.3°C)–390°F (198.9°C). Direct and indirect heated fryers equipped with proper conveyor systems can be used for frying coated products. Immediately after frying, products are frozen in blast freezers using liquid nitrogen and then packaged. The packaged product is stored in the freezer at –5° to –10°F for distribution to restaurants, food services and the supermarkets. The products are shipped in freezer-trucks and stored in freezers at the destination (storage temperature –5° to –10°F). They are taken out of the freezer and fried without thawing. The products in this category are fish, chicken, beef, cheese sticks and vegetables.

In the production of fried fish, the fish arrives at the plant in frozen packages. The product is cut to sizes or the pieces separated. They are coated with batter and dusted with a mixture of starch, dextrose, flavoring, and leavening (for tempura). Batter coating and dusting process is repeated more than once to get better adhesion of the coating. The fish is still frozen. Frying is done at 380°F (193.3°C)–390°F (198.9°C) for sufficient time to set the outer coating. The fish inside is still frozen. The product is then frozen in a blast freezer at –25°F (–32°C) to –30°F (–34°C).

Another category of fish product is fully cooked. This is sold for heating in microwave ovens. The temperature in the interior of the fish must reach 145°F (62.8°C) and then frozen like the others.

In the production of fried chicken and beef, chicken and the beef patties are fully cooked before they are frozen. The oil temperature is the same temperature used for fish frying 380–390°F (193.3–198.9°C). The interior of the product must reach a very specific temperature to prevent the growth of pathogens. This temperature is 160°F (71.1°C) for boneless chicken, 185–195°F (85–90.6°C) for chicken with bones, and 145°F (62.8°C) for beef patties. However, the endpoint temperature for chicken with bones should be 205°F (96.1°C) according to New York City School System to remove the redness from the outside of the bone and the marrow.

Cheese sticks and vegetable sticks are fried in a manner similar to that for the frozen fish. A hard crust is set without affecting the product inside.

Non-coated products such as potato chips, tortilla chips, and corn chips are relatively easy to handle. On the other hand, coated products are different and require more involved handling before and during frying. The reasons may be summarized as: (1) coated products have to go through the batter application and the dusting procedure; (2) product feed to the fryer is also specific to reduce any marriage (joining) of the individual pieces; (3) the interior design of the fryer is critical for conveying the product through the fryer; (4) there must be a submerger for the product that tends to float in the fryer; (5) accumulation of the fines can get burned and impart a dark color to the product and/or burnt flavor to the product; (6) It is important to "set" the outer surface of the coating in hot oil before the product touches the internal conveyor of the fryer. This zone is called the "free-fry" zone, and is located at the beginning of the fryer. This applies to coated products, potato chips and various other fried products. This prevents sticking of the product to the fryer conveyor or to each other (clumping) before the product reaches the frying zone; and (7) the design of the free-fry zone and the in-feed system vary considerably with the product to be fried.

### 12.7.5 French Fries Production

French fries, like meat patties or fish patties, do not float in the fryer. French fries are fried with and without coating. The coated products are also very popular. There are also different cuts. The straight cut is the commonest. The other types of cut are Julienne and spiral.

Although French fries use potatoes with high solid content, potatoes contain 80–82% moisture. This demands high heat load on the fryers. The process for making French fries is very involved.

In the process, the potatoes are washed and then peeled in a steam peeling process. They are cut into $0.290 \times 0.290$ in$^2$ ($7.4 \times 7.4$ mm$^2$) dimensions in water flume using an in-line water knife. Potato strands are washed to remove the surface starch as they are conveyed to a strainer. Excess water is drained through the strainer. The raw potato strands are blanched in a two-stage blancher. Blanching is done at 165°F (73.9°C) for approximately 7 min in the first stage, and at 175°F (79.4°C) for approximately 3 min in the second stage. The blanched product is then soaked for 45–60 seconds in a vat containing 0.6 % sodium acid pyrophosphate solution, maintained at 145°F (62.8°C). This is to provide some firming or strengthening to the potato strands. The soaked product is then passed through a dryer that is operated in three sections, maintained at approximately 83°F (28.3°C). This operation helps equilibration of moisture in the potato strands before frying. The product is fried in a French-fry fryer approximately for 1 min and 5 s, with an oil inlet temperature of 365° F (185°C). Then they are conveyed into a freezer, directly from the fryer. The freezer has two zones, the first zone is typically maintained at −14°F (–25.6°C) and the second zone is maintained at −26°F (–32.2°C). Typical residence time in the freezer is 20 min. The product is collected in containers and stored at −10°F (–23.3°C). They are later packed in paper bags, with plastic inner lining. The packed product is stored back in the same freezer, maintained at −10°F (–23.3°C). Moisture content of the product at this point is approximately 64 to 65% and the oil content is approximately 14 to 18%.

## 12.8 GENERAL REMARKS ON THE PAR-FRYING PROCESS

Par-frying is a good way to produce and supply large amounts of intermediate product to restaurants and food services. This reduces the steps for preparation of products at the restaurants, lowering their cost of food preparation. There are several important aspects of par-frying. It offers large-scale product and distribution capability of intermediate or partially processed foods. In addition, par-fried product absorbs less oil than the fully fried product. Lower oil pick up by the product increases the oil turnover time in the par-fried product fryer, causing high degradation to the oil. This produces a high concentration of free radicals in the fryer oil. The par-fried product absorbs the oil containing a high concentration of free radicals. These free radicals then catalyze the oxidative degradation process of the oil in the product during storage. Subsequently, during final frying of the par-fried product, an exchange of oil takes place between the par-fried product and the frying oil at the finishing fryer. This increases the free radical concentration in the finishing fryer oil, which causes rapid oxidative breakdown of the fryer oil. This is why the par-fried product develops an unpleasant oil flavor when the product is held in a package after finish frying. This oxidation in the product cannot be prevented even when the refried product is packaged in metallized bags with nitrogen flush. The product exhibits a fraction of the shelf-life of the same product fried under normal process (not par fried and refried). Therefore, this process cannot be used for large-scale manufacture of par-fried salty snack food to distribute them to the final processors for refrying and sales.

## 12.9 GENERATION OF FINES AND THEIR REMOVAL

Fines accumulate in the fryer pan during frying. These are primarily carbohydrate material (can be proteinaceous material from poultry, meat or fish). The crumbs get charred during frying. Thus, accumulation of fines can darken the fryer oil. This leads to darker-colored product with a burnt taste. This is why it is necessary to remove the fines from the fryer continuously or at certain frequencies. The coated products generate a lot of fines accumulated at the bottom of the pan.

One can remove the fines from the fryer by using a continuous filtration system. Certain amounts of fines accumulate in the fryer even after using a continuous filter. Fryer sanitation removes the residual fines from the fryer.

A continuous oil filtration system is highly desirable for products that generate large amounts of fines during frying. Indirect-heat fryers with continuous and high oil flow make it easier to remove a large portion of the fines from the fryer via the continuous oil filtration system. However, with very high accumulation of crumbs or sludge, it is recommended to have a set of bottom-dredging bars that push the accumulated fines from the fryer pan into a sump. It is then pumped through a filter to separate the oil from crumbs. The filtered oil is recycled through the fryer with appropriate system design.

Various types of filters are used to remove fines. Paper filters are not the best. They cause high oil loss and also the hot oil is exposed to air for a long period of time. The fryer system generally contains a filter to remove the coarse material from the oil. Sometimes, this is augmented with a finer filter that removes the smaller particles from the fryer oil. In many applications, one needs to use a combination of a motorized and a centrifugal filter (or a rotary drum filter) (Figure 12.8).

The type of filter for a fryer should be carefully chosen based on the size, the amount and the degree of hardness of the fines to be removed from the fryer oil. For products that produce heavy amounts of fines, such as breaded products, and sugar infused products, a bottom-dredging system is used (as described above). This is a specially designed conveyor system. The fryer manufacturer should be informed of the need for heavy fine removal during frying.

Sometimes, a continuous filtration system is used to clean the fryer oil. In this process, it is recommended to take out approximately 5% of the fryer oil, filtered through an in-line filter and returned to the fryer. The flow of oil across the fryer pan is not uniformly distributed due to various factors. This allows fines to accumulate at various locations on the fryer pan and, therefore, cannot be removed by the filter. In reality, a continuous filter will not work satisfactorily if the fines are not carried out of the fryer pan at a uniform manner by the oil.

## 12.10 OIL TREATMENT FOR EXTENSION OF FRY-LIFE FOR THE OIL

Sometimes, the fryer oil is treated in an external system to remove the oil decomposition products. This is usually done at shut down, whether this occurs daily or weekly. This oil treatment process takes out the fines and also treats the oil to reduce free fatty acids, color, oxidized material and soap in the fryer oil.

The oil can be treated in a batch process at the end of frying. The oil from the fryer is transferred into a holding tank from which it is transferred to a slurry tank. The treatment adsorbent is added and mixed into the oil with the help of a mechanical mixer for 10–20 min. The oil is then filtered to remove the adsorbent and then stored in the holding tank. This system is cumbersome to handle. The oil is normally at 240–280°F (115.5–137.8°C) by the time it is treated.



**FIGURE 12.8** Rotary drum oil filter (Courtesy of Heat & Control Company).

The fryer oil can also be treated continuously. In this case, about 5% of the fryer oil is taken out of the fryer every minute through a metering pump. The oil is then passed through a small slurry tank to where metered amount of the treatment adsorbent is added. The oil and adsorbent are mixed well for intimate contact for 10–20 min, continuously filtered through a filter and returned to the fryer. This provides a theoretical filtration turnover time of 20 min for the fryer. The oil temperature is $>280$°F (137.8°C), so the oil may have to be pre-cooled before the addition of adsorbent and the filtered oil may have to pass through a trimming heater to bring the filtered oil to frying temperature to avoid undue drop in the fryer oil temperature. This system is difficult to design but easier to operate.

There are many treatment agents which are commercially available for oil treatment. Although oil treatment can be beneficial, not every treatment material on the market is satisfactory. Some reduce the free fatty acid via acid/base reaction. The base metals in these adsorbents are typically calcium and magnesium salts that react with the free fatty acid, forming calcium and magnesium soaps. These soaps in the oil cause rapid rise in free fatty acid and also cause rapid oil oxidation. Therefore, one must make certain that the reduction of the free fatty acid is not accomplished via an acid/base reaction. Therefore, one must monitor the soap content of the oil before and after the treatment.

Certain manufacturers of the treatment material recommend that it does not have to be removed from the oil. This could become a regulatory issue in many countries because the additive would be considered as an adulterant. Certain manufacturers add antioxidants into the fryer oil. This is also not acceptable in USA and some other countries. Therefore, one has to be careful regarding the selection and use of oil treatment materials.

A second method for treating fryer oil is carried out by filtering the fryer oil through filter pads impregnated with treatment adsorbents. The fryer oil at 280–300°F (137.8–148.9°C) is cleaned of major suspended material in a pre-filter, and then passed through the treatment pad. The passage of the oil through the filters is conducted by using the suction side of a pump connected to the outlet of the filter containing the filter pads to avoid premature plugging of the pores in the filter pads. This method removes soap, trace metals, oxidized and polymerized materials from the oil, but does not chemically react with the free fatty acids or reduce it.

The advantage of the filter pad system is that it is easier to operate. The critical component is the pre-filter. Inadequate removal of suspended solids in the oil can plug up the filter pads and shorten their useful life considerably.

## 12.11 FAMILIARIZATION WITH THE TERMINOLOGY USED IN INDUSTRIAL FRYING

It is essential for the user or potential user of an industrial fryer to know the terminologies used in the frying industry as listed below:

**Fryer Capacity:** Fryer capacity is chosen on the basis of the production volume needed for the business. There are several factors that must be taken into account to determine the actual capacity of a fryer. These are, daily operation of the fryer (8, 16 or 24 hours), frying time to reach the product end-point moisture, fryer cleaning (sanitation) frequency, time for fryer cleaning, fryer start up and shutdown time required,

estimated time for product changeover, company's warehousing and distribution system and required product code date based on the shelf-life and sales and distribution requirements. This information assists the fryer manufacturer to determine the physical dimension of the fryer, belt width and belt loading.

**Belt Loading:** It is the weight of product per unit area of fryer. It is expressed as $lb/ft^2$ or $kg/m^2$ for products like chips or $pieces/ft^2$ or $pieces/m^2$ for meat patties or fish fillet along with a specified weight per piece of product.

**Fryer Size:** Fryer size indicates the number of pounds (or kg) of a product produced per hour in a given fryer. For example, PC 3600 means a continuous potato chip fryer which is capable of producing 3600 lb/h of fried potato chips under standard operating conditions delivering the finished product with the correct endpoint moisture and acceptable texture.

Factors important in determining the fryer size are the desired production rate in lb/h (kg/h), physical dimension of the product, the fry time required (min, s) and belt loading, typically in $lb/ft^2$ ($kg/m^2$).

A number like 3020 indicates that the fryer pan (in a fryer) is 30-inches wide and 20-feet long.

**Cook Area:** Cook area is calculated by multiplying fryer pan width with cook length.

**Cook Time:** It is measured from the time the raw feed enters the fryer and the finished fried product leaves the fryer. This time is dependent on the type of product and the desired moisture content for the final product. This also depends on the fryer design, heat input, and heat recovery time.

**Direct Heating:** The oil is heated by the hot flue gas from the burner. The hot gas passes through the tubes (along the length of the fryer or across the fryer) that are immersed in the bed oil in the fryer pan, or through a heating chamber directly located under the fryer pan with refractory brick lining.

**Indirect Heating:** In indirect heating, the oil is heated by hot thermal fluid that is heated in an external heater and then pumped through several tubes that are immersed in the oil.

**External Heat Source:** The oil from the fryer is pumped out and passed continuously through an external heater and returned to the fryer. The heater can be a high-pressure steam heat exchanger or it can be gas-fired. Gas-fired heaters can be direct or indirect heating type. In directly heated gas-fired heaters, the oil passes through a bundle of tubes and the hot flue gas heats the oil from the outside of the tubes. The oil can get overheated or scorched easily in this type of heating system. In an indirect heating system, the flue gas passes through a tube bundle. Ambient air is forced across these tubes when the air becomes hot. The hot air is used to heat the oil in the tube bundle. This system is gentler and maintains much lower oil-film temperature inside the tubes.

**Oil Film Temperature:** Fluid passing through a pipe forms a film along the inside of the tube. The thickness of this film decreases with increased flow rate of the fluid. Oil temperature at this film is significantly higher than the temperature at the center of the pipe or the mass average temperature of the oil passing through the tube. In direct gas-fired oil heaters, the oil film just inside the pipe wall can be heated to a very high temperature. This damages the oil, resulting in reduced fry life for the oil and reduced product shelf-life, unless this film temperature can be controlled.

In an indirect gas-fired heater, the film temperature can be maintained at a much lower value. This helps maintain better oil quality in the fryer.

**Delta-T:** This is the temperature difference between inlet (feed-end) and outlet (discharge-end) seen in the fryer when it is operated at the designed capacity. When the fryer is idle, the temperatures at the inlet and outlet of the fryer are essentially identical (i.e., Delta-T = 0). A temperature differential is established between the inlet and the outlet of the fryer once frying resumes. For example, the delta-T is 40°F (4.4°C), when the oil inlet temperature is 360°F (182.2°C) and the outlet temperature is 320°F (160°C). The value of delta-T depends on the moisture content of the incoming feed and that of the final product. This temperature differential is critical to achieve the desired product characteristics (dehydration rate, amount of dehydration, development of texture and color).

In an indirect-heat fryer, this temperature differential can be designed into the system to a precise degree. By designing the oil flow through the fryer at a specific velocity range, the energy (heat) absorbed by the product at fryer inlet can produce a predictable temperature gradient (Delta-T) down the length of the fryer.

Most direct-fired fryers have dual-control heat banks (fire-tubes or thermal radiators). These heat banks can be set to different temperature set-points at each end of the fryers which can provide a fairly reliable "Delta-T".

**Oil Turnover Time:** It is the theoretical time required by the product to pick up all the oil from the fryer filled to its designed level in the pan. It is expressed in hours. Oil turnover times for various fryers are listed in Table 12.2; 6.9 or 7.0 hours is considered desirable for designing a tortilla chips fryer. In actual operation, the turnover time is 7.8–8.2 hours. This is because the start up, shutdown, product changeover, and mechanical down time reduce the fryer utilization to 85–90%.

For example, if we use a fryer containing 5,000 lb of oil for frying of 2000 lb/hr of finished product having 36% oil, oil picked by the product and oil turnover time can be calculated as:

$$\text{Oil Picked by the Product} = 0.36 \times 2000 = 720 \text{ lb/hr} \tag{12.1}$$

$$\text{Oil Turnover Time} = \frac{5000 \text{ lb oil}}{720 \text{ lb oil/hr}} = 6.9 \text{ hr} \tag{12.2}$$

**TABLE 12.2**
**Oil Turnover Times for Various Fryers**

| Type of Fryer | Actual Oil Turnover Time (h) |
|---|---|
| Potato chips | 9.5–11.0 |
| Tortilla chips | 6.5–8 |
| Corn chips (extruded product) | 4.0–5.0 |
| Batch (Kettle) fryer | 20–30 or longer |
| Restaurant fryer | 18–20 days |

**Heat Load Requirement:** It is the theoretical amount of heat required to cook a product without considering any heat loses. This is expressed in BTU/lb or J/kg. The fryer manufacturers can provide the net heat loads for individual products. These databases are treated as trade secrets. No published values can be found in the literature.

The primary function of a fryer is to remove the moisture from the product being fried. The fryer oil supplies the sensible heat required to heat the product up to the frying temperature and the heat of vaporization of the free water present in the food.

Most of the heat is needed for vaporizing the free moisture from the product. Potato chips frying requires maximum amount of heat load per unit mass of chips made because potatoes contain 80% moisture and it is reduced to 1.5%. Corn chips and tortilla chips require less amount of heat per unit mass of product fried because the feed moisture is about 50%, and it is reduced to 1% in the finished product. There are several areas in the process where the heat energy is lost. Therefore, the thermal capacity of the fryer must be in excess of the theoretical amount of energy required just for the dehydration and heating of the product. In addition to the energy required to raise the temperature of the feed from room temperature to the frying temperature and to dehydrate the product, the energy required for heating all physical equipment, including the piping, filters, radiation heat loss from the fryer, furnace and other ancillaries, heat loss through the fryer exhaust and heat loss through the gas heater flue, rate of dehydration of the product and thermal efficiency of the heat exchange system must be taken into account in designing the oil heating system.

The typical heat load required for various products are given in Table 12.3. It is quite evident that the heat load can vary considerably between various types of products. As stated earlier, potato chips require the highest amount of heat energy because of the high moisture content of the raw potatoes (> 80% moisture).

**TABLE 12.3**
**Typical Heat Load Required for Various Products**

| Product | Temperature of frying oil (°F) | Heat requirement (BTU/lb) |
|---|---|---|
| Potato chips | 370 | 4500 |
| Tortilla chips | 375 | 1500 |
| Corn chips | 390 | 2250 |
| Batter coated & par-fried products [a] | 375 | 350 |
| Egg rolls & burritos [b] | 355 | 200 |
| Nuts | 325 | 500 |
| Fried snack pies | 365 | 1000–1500 |

[a] Heat is used only for setting the crust and not for cooking the fish inside.
[b] This is only to fry the shell. The filling is pre-cooked.
From: Courtesy of Sea Pack Corporation.

The factors listed below are very critical to establish the heat load required for any frying system.

- "Delta-T", the temperature differential needed across the length of the fryer.
- Heat recovery time (also known as the response time for the heating system to maintain proper oil temperature).
- Minimizing temperature overshoot

**Recovery (Response) Time:** There is a huge demand on the heat energy in the fryer as soon as the raw food enters the fryer. There is loss of heat and a drop in the oil temperature. Recovery or response capability of the heating system means how fast the heat exchanger can bring back the oil temperature to normal when there is an upset. The same phenomenon applies when there is a step increase in the fryer feed rate. Generally, there is a temperature overshoot after an upset in the system. This is influenced by the availability of excess thermal energy beyond the amount of heat required to fry the product and compensate for the losses and the type of heat exchanger used in the system.

Indirect heat external heat exchangers have the fastest response to the change of heat load requirement. These heat exchangers also have the lowest temperature swing, which is typically found to be $\pm 2$°F ($\pm 1.1$°C). This temperature variation can be further reduced by using continuous fresh oil make up and precision oil flow. Direct fired fryers have very slow response rate. These systems take the longest time to heat up or cool down the oil in the fryer. There is always a time lag between the time the set point is changed on the controller and the time the oil begins to indicate any change in temperature. A temperature swing of $\pm 10$°F ($\pm 5.6$°C) to $\pm 15$°F ($\pm 8.3$°C) in the temperature of the fryer oil is not uncommon. Temperature response is more predictable when a thermal fluid radiator is used in a direct heat fryer. This is possible because of the regulated flow of the thermal fluid through the radiator to regulate the heat supply to the tubes. When the internal thermostat in the fryer senses the need for a change in the heat requirement, a control valve regulates the flow of thermal fluid through the radiator. A temperature swing of $\pm 7$°F ($\pm 3.9$°C) to $\pm 10$°F ($\pm 5.6$°C) is commonly seen in this type of heating system.

**Air Requirement (for combustion):** Any combustion system requires air supply at two stages of the combustion system (primary and secondary combustion) to achieve complete combustion of the fuel. The initial mix of the natural gas and the primary air is generally sufficient for the complete combustion of the natural gas. However, the complete combustion of the fuel (natural gas) still requires an additional air supply.

Besides the total amount of air for combustion, the plant needs air supply for the personnel in the working area and for replenishment of air lost through the exhaust system.

**Oil Quality Management:** Oil quality can be better maintained in a continuous fryer compared with a batch fryer. The continuous fryer has a much lower oil turnover time. Oil quality management encompasses a variety of areas, such as: (1) setting fresh oil quality standards; (2) deodorized oil storage; (3) truck loading;

(4) oil-receiving procedure; (5) oil unloading and storage procedure; (6) fryer start-up procedure; (7) fryer operation; (8) fryer shutdown procedure; (9) fryer sanitation procedure; (10) temporary fryer shutdown procedure; (11) product packaging; and (12) fryer oil treatment for better oil performance.

The oil quality program starts with the receipt of highest quality oil from the supplier. Guidelines for some of the critical oil quality parameters are given in Table 12.4.

Oil loading at the refinery, method of oil transport and oil unloading and storage play a significant part in the performance of the oil in frying and the desired product shelf-life.

Fryer start up, operation, shutdown, temporary fryer shutdown and the fryer sanitation process can affect the fryer oil quality and product stability. Undue delay at start-up while the heated oil is waiting in the fryer is detrimental to oil quality. Non-steady production throughput damages the oil. Frequent fryer shutdowns are highly undesirable for good oil quality and product stability. Therefore, a fryer should be started and operated at full capacity until it is time to shutdown the production for the week. A long fryer shutdown procedure without cooling the oil can be very damaging to oil quality. Incomplete removal of the alkali used in sanitation can rapidly increase hydrolysis and oxidation of the fryer oil at the next start-up.

Most commercial frying operations monitor the free fatty acids in the fryer oil to determine its quality. Hydrolysis is not the only reaction that goes on in the fryer oil. Therefore, measurement of free fatty acids may not provide the complete picture on oil quality in the fryer. Some of the oxidation products should also be analyzed to get a complete picture on the oil quality in the fryer at any given time. Some manufacturers analyze their fryer oils for para anisidine value (pAV), polar material (PM) and polymers. Others focus on free fatty acids and PM analysis. There is no general rule for oils from fryers of every type of product because shelf-life prediction cannot be made for every product based only on one oil quality parameter.

The oil quality in frying is better managed by operating the fryer at its designed capacity and for long hours at a time. The fryer should be shutdown only for sanitation at the end of the week's production, product changeovers and unforeseen mechanical issues.

Fry life of the oil is further improved by timely and proper sanitation of the frying system. This involves washing the frying system with caustic or sanitation

**TABLE 12.4**
**Standards for Quality Parameters of Refined, Bleached and Deodorized Oil for Frying**

| Analytical parameters | Limits/standards |
|---|---|
| P (Phosphorus) | Preferably $<0.5$ ppm and not $>1$ ppm |
| PV (Peroxide value) | $<1$ meq/kg, preferably $<0.5$ meq/kg |
| pAV (para anisidine value) | $<6$, preferably $<4$ |
| $Fe^{++}$ | $<0.5$ ppm, preferably $<0.3$ ppm |
| $Ca^{++}$ | $<0.5$ ppm, preferably $<0.2$ ppm |
| $Mg^{++}$ | $<0.5$ ppm, preferably $<0.2$ ppm |

chemicals, rinsing and neutralization of the residual soap or caustic left in the system after rinsing the fryer post the caustic wash.

**Fryer Sanitation:** The hood and other inaccessible parts of fryer are equipped with spray nozzles as part of the cleaning in place (CIP) system installed by the fryer manufacturers. The CIP systems are common with equipment designed for operation in the plants processing meat, poultry or fish, where daily sanitation of the frying system is mandatory. However, the fryer pan, the piping and the external oil heater must be washed with caustic solution or sanitizing chemical to remove the residual oil and crumbs left after the fryer is emptied.

Logistics for specific types of fryer may vary depending upon the type of the fryer and the product it fries. For example, a direct fired fryer with no oil recirculation will require more manual cleaning compared to that with an oil re-circulation pump because the pump can move the caustic solution through the entire system. Similarly, a kettle fryer will require manual scrubbing for sanitation, while a continuous potato chips fryer can use the recirculation pump to get the cleaning action.

Fryer sanitation is essential for maintaining the fryer oil quality. Any amount of residual oil as well as crumbs or caustic, can catalyze the oil degradation reactions.

## 12.12 CONCLUSIONS

Par-frying has become a significant part of the frying industry. This has provided the convenience and economic benefit to the restaurant and the food service sectors.

The customers at restaurants and food services consume the fried products soon after their preparation. Therefore, shelf-life of the par-fried products after full frying is not a significant factor. On the other hand, the industrial products are sold in various types of packages that protect the products from becoming rancid during storage and distribution under ambient condition. The oil in the restaurant fryer degrades rapidly due to the constant exposure to high temperature and the extended hours of idle time. The continuous fryer generally maintains better oil quality. However, frequent fryer shutdowns, poor start-up, operation, shutdown practices, lack of sanitation or absence of sanitation and over-heating of the oil can cause rapid degradation. Kettle fryers are gentler on the oil than the restaurant fryers, but are significantly poorer than the continuous fryers because of the long oil turnover time. Proper oil management program can improve the fry life of the oil which can enhance the shelf-life of the fried products.

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# 13 Alternative Frying Technologies

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## CONTENTS



## 13.1 INTRODUCTION

Conventional fryers used in industry can be categorized into two types: batch fryers and continuous fryers. Batch fryers are used in restaurants and can produce fried products on a small scale. Oil is put into a pan and heated by a gas burner. It may also be heated by using a heat exchanger. After the oil is heated to the desired temperature, a basket filled with food is lowered into the hot oil. The addition of food causes a drop in oil temperature, but then oil regains its initial temperature as frying continues. In continuous fryers, food enters the fryer at one end and fried product is removed from the opposite end. These fryers are used for large-scale production of fried products (Gupta, Grant, and Stier 2004).

Deep-fat frying is carried out at high temperatures (about 180°C). Surface darkening and consequently higher acrylamide formation may occur due to high temperatures. Considerable oil uptake is observed during frying. Demands for reducing oil content of fried foods are growing because of health concerns. In addition, investigating the ways to reduce acrylamide formation is one of the main topics in frying research in recent years. It is well known that, in addition to the raw material properties, frying methods and conditions affect product quality. Therefore, alternative ways such as vacuum frying, pressure frying and microwave frying are being studied to improve the quality of fried foods.

In this chapter, the principles and recent progress in vacuum and pressure frying will be discussed. In addition, information about the usage of microwaves for frying, which is a recent alternative technology, will also be given.

## 13.2 VACUUM FRYING

Vacuum frying is carried out at pressures below atmospheric levels, which lowers the boiling points of oil and moisture in the foods. Therefore, frying can be achieved at lower temperatures. In Europe, vacuum fryers are used to produce French fries because it is possible to achieve the necessary moisture content without severe darkening of these products (Moreira, Castell-Perez, and Barrufet 1999).

Vacuum frying offers some advantages such as reduction in oil uptake, and preservation of natural color and flavor of the product due to lower temperature and absence of air during the process and preservation of oil quality for longer times (Shyu, Hau, and Hwang 2005). However, vacuum frying operations are usually done in closed vessels, and therefore suffers from the disadvantages common to batch processes. Continuous vacuum fryers are also available, but they are extremely costly (Gupta, Grant, and Stier 2004).

In vacuum frying, oil is heated by circulating it through an external heater. The food is placed in a basket, and the basket is placed in the vacuum chamber above the surface of the oil. After vacuum is applied, the basket is lowered into the hot oil. Oil temperature drops with the addition of food, but then oil regains its initial temperature as frying continues. After frying, fryer is vented and the vacuum is broken slowly. Excess oil is allowed to drain and the product is removed.

### 13.2.1 Mechanism of Vacuum Frying

Frying can be defined as the process of drying and cooking through contact with hot oil. There are three distinct periods in drying of foods. These periods are also observed in frying process. However, there are some differences depending on the type of frying, such as conventional and vacuum frying (Garayo and Moreira 2002).

1. Initial heat-up period: The wet solid material absorbs heat from the surrounding media. The product is heated-up from its initial temperature to a temperature where the moisture begins to evaporate from the food. In vacuum frying, this period is very short and therefore difficult to quantify. The boiling point of water is lower in vacuum frying due to the lower pressure. Therefore, the product is heated-up from its initial temperature to the boiling point of water in a very short period of time.
2. Constant rate period: The surface of the solid is initially wet and this period continues as long as the water is supplied to the surface as fast as it is evaporated. The rate of mass transfer is limited by the rate of heat transfer. Constant rate period could not be observed in vacuum frying of potato chips (Garayo and Moreira 2002).
3. Falling rate period: This period appears in atmospheric and vacuum frying. The entire surface is no longer wet; the plane of evaporation slowly recedes from the surface. The amount of moisture removed in this period may be relatively small, but the required time may be long.

The mass transfer in atmospheric frying can be analyzed by dividing the process into two periods: during frying and during cooling. During frying, product temperature rises to the boiling point of water and water within the sample vaporizes. Temperature and pressure within the sample increase at a fast rate. During this period, capillary pressure is negligible. During cooling period, oil adhered to the surface of fried product penetrates into the pores because the pressure inside the pores changes as a consequence of capillary pressure rise (Moreira and Barrufet 1995). In the case of vacuum frying, there is a pressurization period between frying and cooling periods (Garayo and Moreira 2002). During the frying period, capillary pressure is negligible, as in the case of atmospheric frying, therefore oil absorption in this period is negligible. When the product is removed from the frying oil and the vessel is vented, the pressure in the sample rises to atmospheric levels. During this stage, air and surface oil are carried into the empty pores. As the sample is removed from the oil, the adhered oil intends to flow into the pores during pressurization period. An increase in the surrounding pressure at constant temperature, during the pressurization period, causes the vapor inside the pores to condense. As the water vapor condenses, oil penetrates into the pores due to the pressure difference. However, the penetration of oil into the pores may be obstructed if the diffusion of gas is faster. During the cooling period, part of the adhered oil penetrates into the pores, as in atmospheric frying.

In vacuum frying, the pressurization period has an important role in oil absorption. Oil absorption may decrease or increase depending on the amount of surface oil and free water in the product.

### 13.2.2 Recent Studies about Vacuum Frying

Garayo and Moreira (2002) studied the effect of oil temperature (118, 132, 144°C) and vacuum pressure (16.661, 9.888 and 3.115 kPa) on the drying rate and oil absorption of potato chips, and also on product quality attributes such as shrinkage, color and texture. Oil temperature and vacuum pressure had a significant effect on the rates of drying and oil absorption in potato chips. Vacuum pressure and rate of moisture loss were negatively correlated. The water in the potato chips begins to vaporize faster at a higher vacuum level because lower pressure means a lower boiling point of water. Higher vacuum levels lead to faster development of crust and thus to faster oil absorption rate due to loss of characteristic hydrophilicity of raw potatoes during the process. Final oil content of the chips was not significantly affected by oil temperature and vacuum pressure level ($p < 0.05$) but was affected from the frying time and the remaining moisture. Final oil content was higher for potato chips fried under atmospheric conditions as compared with potato chips fried under vacuum. Potato chips fried under vacuum had higher volume shrinkage, lighter color and softer texture than potato chips fried under atmospheric conditions (Garayo and Moreira 2002). Less shrinkage was observed when lower vacuum pressure and higher temperature was used. Oil temperature and vacuum pressure did not have a significant effect on color and texture ($p < 0.05$).

Vacuum frying was suggested as an alternative process to produce chips with lower acrylamide levels (Granda and Moreira 2005). Acrylamide content of chips fried under vacuum was reduced by 94% as compared with those fried to the same

moisture content under atmospheric conditions. Different trends were observed in the acrylamide formation during vacuum frying and conventional frying. During conventional frying, the acrylamide content in potato chips increased with frying time and eventually leveled off. The leveling off was explained by the degradation of acrylamide with increasing time and temperature. In vacuum frying, the acrylamide content in potato chips continued to increase with frying time.

Shyu and Hwang (2001) studied the effects of processing conditions and immersing the blanched apple slices in fructose solution as a pretreatment on the quality of vacuum fried apple chips at $< 98.66$ kPa. Moisture content, lightness (L) and breaking force of apple chips decreased as frying temperature and time increased, while the color difference ($\Delta E$) and oil content increased during vacuum frying. Moisture content, oil content, color and texture of apple chips were significantly affected by frying temperature, time and concentration of fructose ($p \leq 0.05$). The optimal conditions were found to be vacuum frying at 100–110°C, for 20–25 min after immersing the apple chips in fructose solution of 30–40% concentration when the breaking force was considered as a quality indicator.

Fan et al. (2005b) studied the effects of processing conditions (frying temperature, vacuum pressure and frying time) on the moisture, oil contents and texture of fried carrot chips. The optimal conditions were found to be vacuum frying at a temperature of 100–110°C, at a vacuum pressure of 0.010–0.020 MPa for 15 min using the oil content and breaking force as quality indicators. Frying temperature, vacuum pressure and frying time significantly affected moisture content, oil content and texture ($p < 0.05$). Moisture content and the breaking force decreased, but the oil content increased with decrease in vacuum pressure and increase in frying time and temperature (Fan et al. 2005b). Lower vacuum pressure increased the rate of moisture removal and oil uptake during frying ($p < 0.05$). Moisture and oil contents of the carrot chips were found to be affected by the vacuum temperature and frying time. Color was not affected from frying temperature and vacuum level (Fan, Zhang, and Mujumdar 2005).

The effects of pretreatment and vacuum frying conditions on the quality of carrot chips were studied by Shyu, Hau, and Hwang (2005). Blanched carrot slices were studied at different pretreatment methods before frying: immersion into fructose solution at 50°C for various times (1, 30, 60, 180 min); immersion in fructose solution and then freezing at –30°C overnight; immersion in fructose solution, freezing and then thawing; freezing, thawing and then immersion in fructose solution. In vacuum frying, vacuum pressure was kept constant at 98.66 kPa and the effects of frying temperature (70, 90, 100 and 110°C) and frying time (5, 10, 15, 20, 25 and 30 min) were studied. It was observed that moisture and oil contents of carrot chips were significantly reduced when carrot slices were immersed in fructose solution for 30 min, frozen and then vacuum fried ($p < 0.05$). It was possible to produce carrot chips with lower moisture and oil contents as well as with good color and crispy texture by means of vacuum frying at 90–100°C for 20–25 min.

Fan, Zhang, and Mujumdar (2006) also studied the effects of pretreatments on quality of carrot slices in vacuum frying. Carrot slices were subjected to different pretreatments prior to vacuum frying, which were blanching; blanching and air drying; blanching and osmotic dehydration; and blanching, osmotic dehydration

followed by freezing. These pretreatment methods significantly affected the total yield, carotenoid and vitamin C contents, color, moisture and oil contents and water activity of carrot chips ($p < 0.05$). There was no significant difference in the breaking force of carrot chips produced with different pretreatment methods. The highest yield and lowest oil content was observed in the carrot chips vacuum fried after blanching and osmotic dehydration.

Moisture sorption isotherms of vacuum-fried carrot chips were prepared at 10, 25 and 40°C (Liu-Ping et al. 2005). Peleg, Halsey and GAB models showed good agreement with the experimental data over the entire range of water activity. Smith model was shown to give good fit to the experimental data in the water activity range of 0.32–0.95. The experimental data with water activity values of < 0.50 could be well-fitted to the BET model.

Vacuum frying was also used in the frying of donuts and the effects of initial moisture content of the dough, vacuum pressure (3, 6 and 9 kPa) and frying temperature (150, 165, 180°C) on the required frying time and physical properties of donuts (volume, color, texture, moisture and oil contents) were studied (Tan and Mittal 2006). Higher initial moisture content provided the product with lower volume and oil content, higher moisture content and lighter color. Frying time changed depending on the frying temperature, but it was not affected by vacuum pressure. Donuts with higher volume were obtained when fried under higher vacuum and lower temperatures. Oil uptake increased with increase in vacuum and decrease in frying temperature. The total color change increased with increase in frying temperature, but was not affected by vacuum level. Higher vacuum level and lower frying temperature provided a less compact and firm product. Frying at 180°C under a 3k Pa vacuum was considered to be the desired conditions for vacuum frying of donuts. Oil uptake was higher in vacuum frying of donuts as compared with that in atmospheric frying (Tan and Mittal 2006). However, lower oil uptake was observed in vacuum-fried potato chips as compared with conventionally fried chips (Garayo and Moreira 2002). This may be due to the difference in the amount of oil adhered to the surface of the product.

## 13.3 PRESSURE FRYING

In pressure frying equipment, pressure is generated inside the fryer by the moisture released from the food (Innawong et al. 2006). Therefore, these fryers have limited applications when a large food load is used. On the other hand, it is known that tender and juicier fried products are obtained when pressure frying was used as compared with frying at atmospheric pressure (Malikarjunan, Chinnan, and Balasubramaniam 1997; Rao and Delaney 1995). Recently, nitrogen gas was used as a new pressure generation source in the fryers (Innawong et al. 2006). It was found that the time to reach the specified pressure was significantly shorter when nitrogen gas was used as compared with fryers in which pressure was obtained using steam released from foods. When nitrogen gas was used, the time to reach the pressure of 163 kPa and 184 kPa was < 5 s. When steam released from foods was used in frying, the time to reach 163 kPa and 184 kPa ranged from 90 s to 195 s, and 113 s to 230 s, respectively. The increase in pressure resulted in more moisture retention. The fat

content of crust of chicken nuggets was lower when frying was done at higher pressures. Products fried with lower pressure resulted in a more porous structure, which resulted in higher oil uptake. There was no significant difference between different pressure sources on affecting the fat content of the crust. Frying using nitrogen gas resulted in more tender products.

Ballard and Mallikarjunan (2006) studied the effects of different pressure sources (nitrogen and steam) and different coating materials (methylcellulose and whey protein isolate) on the crispness of chicken nuggets. Chicken nuggets were fried under a constant pressure of 163 kPa at 175°C for 240 s. Using a nitrogen source resulted in crispier uncoated and methyl cellulose-coated products. However, whey protein isolate-coated samples were crispier when they were fried by using steam as compared with nitrogen gas. The authors explained this difference by the effect of different pressure sources on the film-forming property of whey protein isolate, and suggested that further research was needed to explain the phenomenon.

## 13.4 MICROWAVE FRYING

Microwave heating can be used in various food processes such as baking, drying, and thawing. The major advantages of microwave processing are short processing time and energy efficiency. Using microwaves for frying of foods to improve the quality of fried products can be a good alternative to conventional frying.

### 13.4.1 Principles of Microwave Heating

When microwaves interact with a food material, heat is generated inside the food. After the heat is generated, it is transferred by conduction within the food. The generation term is shown by Equation 13.1 (Datta 1990);

$$Q = 2\Pi\varepsilon_0\varepsilon'' fE^2 \tag{13.1}$$

where, Q is rate of heat generated per unit volume, $\varepsilon_0$ is dielectric constant of free space, $\varepsilon''$ is dielectric loss factor of the food, $f$ is the frequency of oven and $E$ is the root-mean-squared value of the electric field intensity.

There are two major mechanisms responsible for microwave heating of foods: dipolar rotation and ionic interaction. In the dipolar rotation mechanism, polar molecules rotate in an electromagnetic field and try to line-up with the field. Because the field is changing its direction depending on the frequency of the oven, the rotation of the polar molecules continues and during this motion they collide with the rest of the molecules. As a result, the rest of the molecules are set-up into motion and kinetic energy arises. Thus, heating takes place.

In the ionic conduction mechanism, the ions try to line-up with the direction of the electromagnetic field. Positive ions will move in the direction of the electromagnetic field, while the negative ions will move in the opposite direction. The change in the direction of the field causes the ions to move back and forth. During this movement they collide with the rest of the molecules and friction occurs, which results in heating of the food.

In microwave heating, internal heat generation increases moisture vapor generation inside the food which can generate significant internal pressure. The resulting pressure gradient is an important mechanism for moisture transfer (Datta 1990). The general equation for moisture transfer during microwave heating includes the terms of moisture movement due to concentration and pressure gradients:

$$\frac{\partial M}{\partial t} = \alpha_m \nabla^2 M + \alpha_m \delta_p \nabla^2 P \tag{13.2}$$

where, $M$ is the moisture content (liquid and vapor phases), $P$ is the pressure, $\alpha_m$ is the moisture diffusivity and $\delta_p$ is the pressure gradient coefficient.

### 13.4.2 Application of Microwaves in Frying

In conventional deep-fat frying, heat is transferred by convection from the hot oil to the food material being fried and by conduction through the solid food. If the frying is done using microwaves, there is also a heat generation within the food. This results in shorter frying time. Because foods contain significant amount of water, heat generation inside the product is due to dipolar rotation. Ionic conduction is also important for microwave frying if the food to be fried contains high amount of ash.

Pressure gradient in microwave heating is very high as compared with conventional heating or frying. The pressure in conventional heating is almost atmospheric pressure. In frying, the maximum value of pressure can be seen near the evaporation front (Datta 2007). Near the surface, the pressure builds up quickly. However, as the surface dries out, pressure decreases. The pressure build-up in frying is small (only 1 kPa) but its effect on moisture transport is important. Convective and capillary diffusional fluxes for water are important in the core region. In the crust region, the magnitudes of convective vapor flux and diffusional vapor flux are comparable, thus the convective term is important.

Microwave frying should be done in a container made of a material that transmits microwaves. To achieve frying in a microwave oven, oil at room temperature is heated to the frying temperatures using microwaves. Then, the food is placed in heated oil and frying is carried out at the desired power level for a specified frying time.

There is a recent patent for combined microwave frying apparatus (Cheng and Peng 2006). This apparatus contains a frying device including housing with an oil groove and a microwave generating device. The aim of this invention is to provide uniform heating in the food and to save oil. It is stated that a typical frying device includes an oil groove for receiving oil and uses gas or electricity for heating the frying oil. The disadvantages of this method are non-uniform heating and deterioration of oil at high temperatures. When several magnetrons are placed inside the frying device and located below the oil groove, microwaves supply an additional heating source. Thus, food can be heated more uniformly and frying time is shortened.

Oztop, Sahin, and Sumnu (2007b) investigated the effects of processing conditions on quality of microwave fried potatoes. Moreover, in this study, the effects of different oil types on the quality of fried products were studied. For all of the oil types, the increase in microwave power increased the moisture loss during frying. Figure 13.1

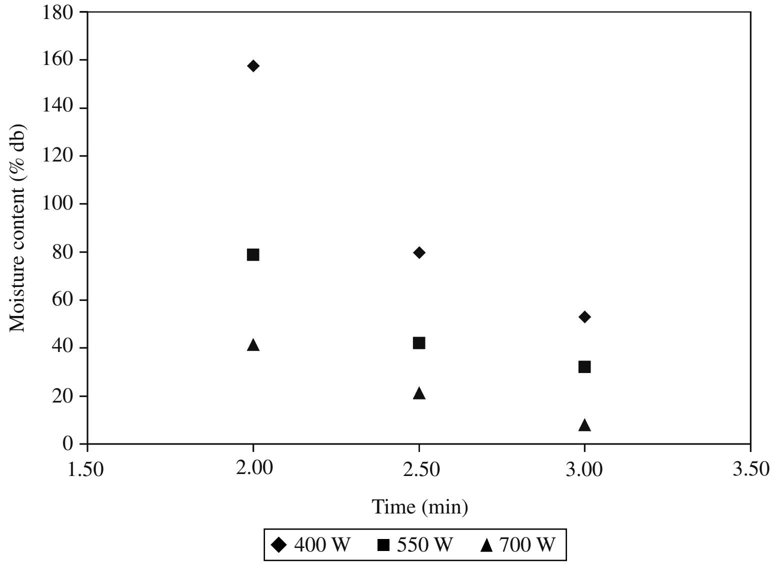



**FIGURE 13.1** Variation of moisture content of potatoes fried in sunflower oil at different microwave power levels (From Oztop, M. H., Sahin, S., and Sumnu, G., *Journal of Food Engineering*, 79. Optimization of microwave frying of potato slices by Taguchi technique, 83–91, 2007b. With permission from Elsevier).

shows the variation of moisture content of potatoes fried in sunflower oil with respect to different power levels. The high power means food is exposed to more microwaves, which increases the pressure gradient and loss of moisture. As microwave power and frying time increased, the oil content of microwave fried potatoes also increased (Figure 13.2). High moisture loss at high power levels may have resulted in higher oil uptake. The comparison of quality parameters of microwave and conventionally fried potatoes is shown in Table 13.1. Microwave-fried potatoes had similar color and texture values with conventionally fried potatoes. However, microwave-fried potatoes lost more moisture as compared with conventionally fried ones. As explained in Section 13.4.1, the high amount of internal heat generation in microwave frying results in a high pressure gradient, which pushes the moisture out of the fried product to a great extent.

Oil contents of microwave-fried potatoes were lower than the ones fried in conventional fryer due to the shorter processing time in microwave frying (Table 13.1). Oil uptake depends on the product type in microwave frying. Although oil uptake was lower in microwave-fried potatoes (Oztop, Sahin, and Sumnu 2007b), higher oil contents were observed in the coating parts of the microwave-fried chicken fingers in comparison with conventional deep fat frying (Barutcu, Sahin, and Sumnu 2007).

Osmotic dehydration is used as a pretreatment of conventionally fried foods to reduce the initial moisture content and as a consequence oil uptake. During osmotic dehydration, water diffuses out of the product while the solute in the concentrated salt or sugar solutions diffuses into the product. Krokida et al. (2001) showed that osmotic dehydration had a significant effect on oil and moisture content of French fries. The effect of osmotic dehydration on the quality of microwave-fried potatoes was studied

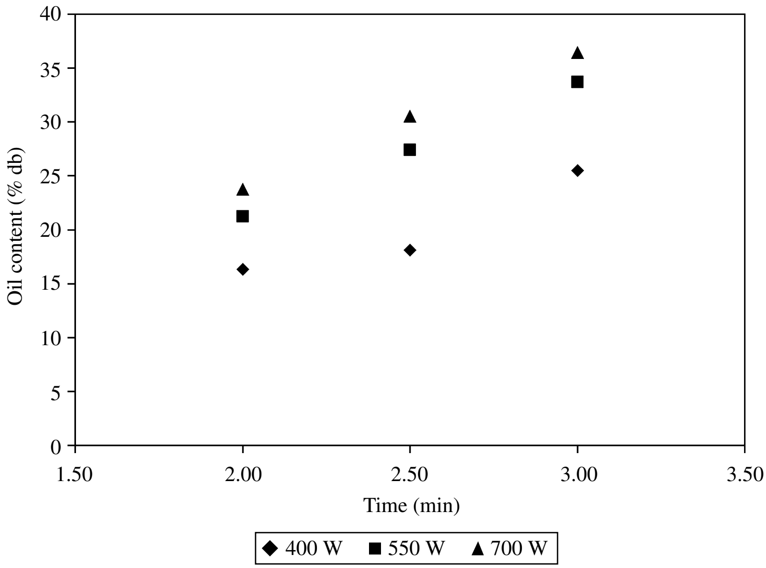



**FIGURE 13.2** Variation of oil content of potatoes fried in sunflower oil at different microwave power levels (From Oztop, M. H., Sahin, S., and Sumnu, G., *Journal of Food Engineering*, 79. Optimization of microwave frying of patato slices by Taguchi technique, 83–91, 2007b. With permission from Elsevier).

**TABLE 13.1**
**Comparison of the Quality of Fried Potatoes Fried in Optimal Conditions for Microwave Frying (170°C, 550 W, 2.5 min) and Conventional Frying (170°C, 4.5 min)**

| Quality parameters | Microwave frying | Conventional frying |
|---|---|---|
| Moisture content (% db) | 42.04 | 67.440 |
| Oil content (% db) | 27.40 | 41.280 |
| ΔE | 45.51 | 49.075 |
| Hardness (N) | 1.51 | 1.637 |

*Source:* Oztop, M. H., S. Sahin, and G. Sumnu. 2007b. Optimization of microwave frying of potato slices by Taguchi technique. *Journal of Food Engineering*, 79: 83–91. With permission from Elsevier.

by Oztop, Sahin, and Sumnu (2007a). The application of osmotic dehydration reduced moisture and oil contents of fried potatoes. However, the hardness values of microwave fried potatoes were higher than conventionally fried potatoes when osmotic dehydration was applied prior to frying.

To understand the effect of salt which diffused into the potatoes during osmotic dehydration, frying was also done by reducing the initial moisture content of potatoes to the same level by conventional drying (Oztop 2005). Higher moisture loss took place when the initial moisture content of potatoes was reduced by osmotic

dehydration instead of conventional drying. This was explained by the diffusion of salt into the product in osmotic dehydration. Because the dielectric loss factor of salt containing foods are high, the heating rate increases, which results in higher moisture loss. The difference in heating rate of osmotically dehydrated and conventionally dried microwave-fried potatoes can be observed by looking at the center temperature of potatoes during frying (Figure 13.3). It was also shown in another study that the dielectric properties of tomatoes increased when osmotic salt solution was used (De los Reyes et al. 2007).

The effects of microwave frying on acrylamide content of potatoes were studied by Sahin, Sumnu, and Oztop (2007). When the acrylamide content of microwave and conventionally fried potatoes having similar moisture contents were compared, there was a 74.4% decrease in acrylamide content in microwave fried potatoes at 550 W as compared with conventionally fried ones. By reducing the microwave power level to 400 W, it was possible to achieve a reduction in acrylamide content by 87.85%. The short processing time can explain the reason for the reduction of acrylamide content of potatoes by microwaves. The decrease in microwave power and frying time were found to be significant for decreasing the acrylamide content of microwave fried potatoes (Sahin, Sumnu, and Oztop 2007) (Figure 13.4). When microwave power increases, the potatoes are heated faster and more acrylamide is formed.

Sahin, Sumnu, and Oztop (2007) in the same study investigated the effects of osmotic treatment on acrylamide content of microwave-fried potatoes. As an osmotic treatment, salt solution (50 g/kg) at 30°C was used. Osmotic pretreatment reduced the acrylamide content of microwave- and conventionally fried potatoes (Figure 13.5). This was explained by the leaching of glucose, fructose and asparagines during osmotic dehydration. Although the moisture content of microwave fried potatoes (at 400 W

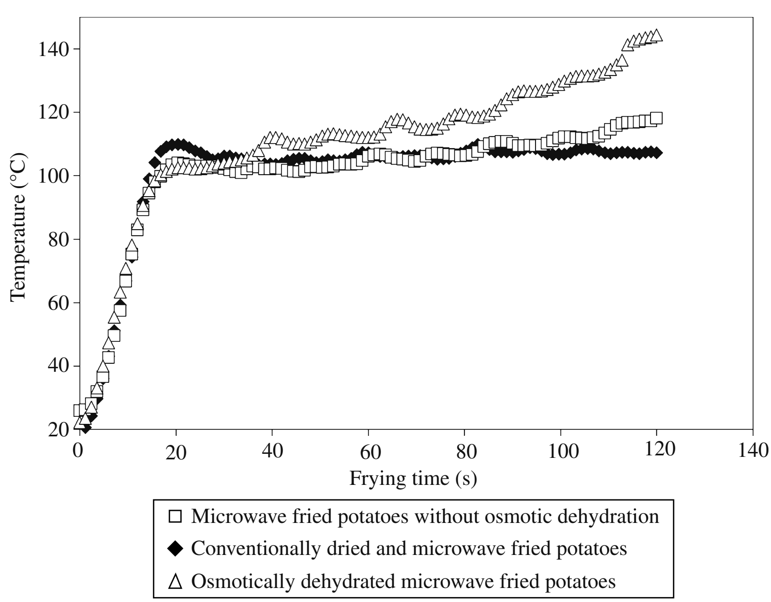



**FIGURE 13.3** Comparison of center temperature of potatoes during different frying methods.

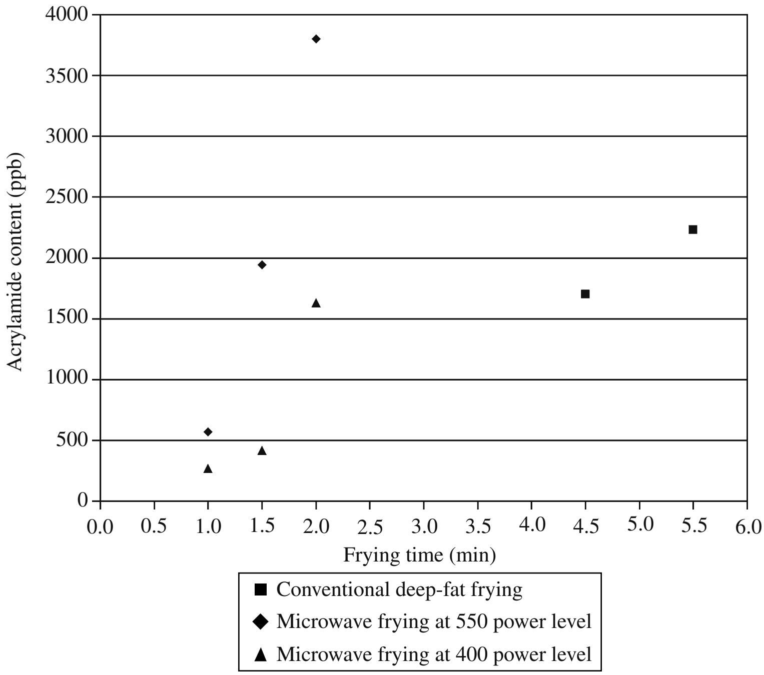



**FIGURE 13.4** Variation in acrylamide content of potatoes fried under different conditions. (From Sahin, S., Sumnu, G., and Oztop, M. H., *Journal of the Science of Food and Agriculture,* 87. Effect of osmotic pretreatment and microwave frying on acrylamide formation in potato strips, 2830–2836, 2007. With permission from Wiley Interscience.)

for 1 min) were comparable with conventionally fried potatoes (at 170°C for 4.5 min), the acrylamide content of microwave fried potatoes were significantly lower than that of conventionally fried potatoes. Short processing time was the reason for this result. However, when osmotic dehydration was applied, the difference between acrylamide contents of microwave- and conventionally fried potatoes became insignificant. Salt is known to increase the dielectric loss factor of foods. Higher loss factor means more heating in microwave oven, which may be the reason for the similar acrylamide content of microwave and conventionally fried potatoes when osmotic dehydration was applied.

## 13.5 CONCLUSIONS

Alternative technologies can be used to improve the quality of fried products. Vacuum frying is an efficient method to reduce the acrylamide content of product. In vacuum frying, the pressurization period has an important role in oil absorption. Oil absorption in vacuum-fried products may be lower or higher as compared with conventionally fried products, depending on the type of the product.

Tender and juicier fried products are obtained when pressure frying is used as compared with frying at atmospheric pressure. Lower oil uptake can be obtained at higher pressures. In pressure fryers, desired pressure can be generated with the steam released from foods. Nitrogen gas has recently been used as a pressure source in these fryers.

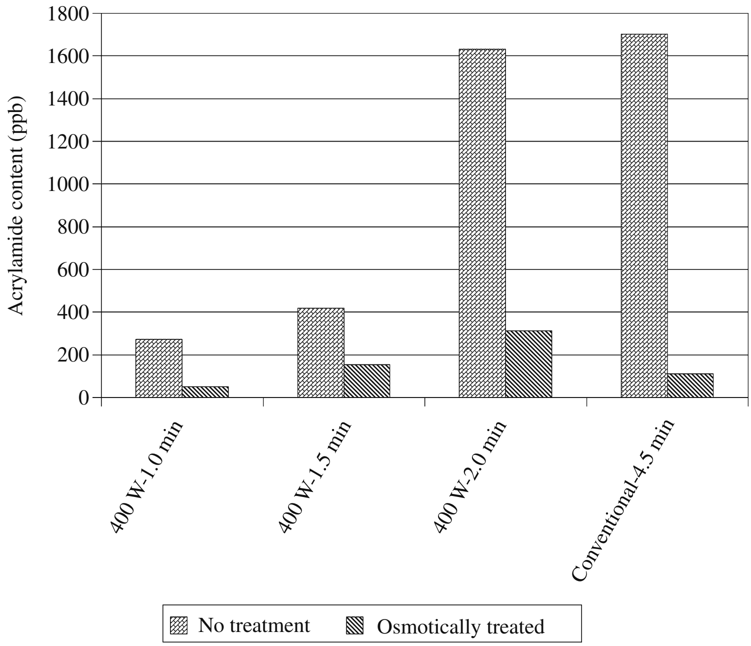



**FIGURE 13.5** Effect of osmotic treatment on acrylamide content of potatoes fried under different conditions. (From Sahin, S., Sumnu, G., and Oztop, M. H., *Journal of the Science of Food and Agriculture,* 87. Effect of osmotic pretreatment and microwave frying on acrylamide formation in potato strips, 2830–2836, 2007. With permission from Wiley Interscience.)

Microwave frying is another alternative to conventional frying to improve the quality of fried potatoes. However, oil uptake in microwave fried products may be lower or higher as compared with conventionally fried products depending on the type of the product, as in the case of vacuum frying. Lower oil and acrylamide containing potato strips can be produced using microwaves. When osmotic dehydration is used as a pretreatment, usage of microwave frying may not be so advantageous as compared with conventional frying.

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**Food Science and Technology**

Battered fried foods consistently remain in high demand despite concerns about their health aspects, prompting food processors to develop new methods and alternative oils and batters in the name of healthy, tasty fried foods and high-performance, cost-effective frying oil. With contributions from an international panel of food technology authorities, **Advances in Deep-Fat Frying of Foods** provides straightforward background on the engineering aspects of deep-fat frying, discusses flavor acquisition during frying, and delineates novel frying technologies employed to make fried foods healthier.



With the aid of numerous tables and illustrations, this concise reference:

- Reviews heat and mass transfer between fried food and the frying medium
- Describes oil uptake mechanisms especially during cooling
- Combines engineering principles with biochemistry to explain the frying process
- Describes alternative techniques, such as microwave frying and vacuum frying, for increased nutritional value
- Discusses flavor acquisition during frying
- Addresses acrylamide, a newly discovered potential carcinogen formed during frying, and considers ways to reduce it
- Examines changes in fried products both at the macroscopic and microscopic levels

As long as they are in demand, food processors will continue to produce fried foods. **Advances in Deep-Fat Frying of Foods** demonstrates how to keep up with demand while ideally making fried foods healthier, tastier, and economically more viable.

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